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H. O. HOFMAN

PROFESSOR OF METALLURGY, MASSACHUSETTS
INSTITUTE OF TECHNOLOGY

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METALLURGY OF MINOR METALS

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METALLURGY OF ZINC AND CADMIUM

BY

H. O. HOFMAN, E. M., MET. E., PH. D.

PROFESSOR OF METALLURGY IN THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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PREFACE

The original plan was to write a volume which should treat of Zinc and Minor Metals. In working, it soon became apparent that a single volume covering the whole subject would be too large and cumbersome; it was therefore decided to issue Zinc and Cadmium separately and make of Minor Metals a special volume. The treatise of zinc and cadmium of 332 pages covers a subject of sufficient importance to be issued separately. There exist a few handbooks treating of zinc and cadmium, but the metallurgy of the two metals has made such progress in recent years that the older manuals do not cover the subject adequately; there is a demand for a work that does this from a chemical as well as a technical point of view. The new data in regard to the physics and chemistry are scattered through the literature. Indications as to the progress made in the technology are found here and there, but visits to plants and conferences with the acting metallurgists is necessary if a true representation of actual practice is to be obtained. I have visited the works of the American Smelting & Refining Co., American Steel & Wire Co., American Zinc & Chemical Co., American Zinc, Lead & Smelting Co., Anaconda Copper Mining Co., Bartlesville Zinc Co., Edgar Zinc Co., Illinois Zinc Co., Matthiessen & Hegeler Zinc Co., Mineral Point Zinc Co., National Zinc Co., New Jersey Zinc Co., U. S. Zinc Co., and have gained an insight of modern ways. I want to express my thanks for the courtesies shown me by the managers, superintendents and other officers of the various companies during my visits of the plants; for the assistance given me later by correspondence when working out details; and for the favor shown by different manufacturers in placing at my disposal numerous drawings. I acknowledge gratefully the assistance of my Colleague, Professor C. R. Hayward, in passing the proof through the press. If it were not for all the help I received, I could not have prepared a treatise that would meet the demands of metallurgists as I hope the present one will.

H. O. HOFMAN.

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PART I

METALLURGY OF ZINC

CHAPTER I

INTRODUCTION

1. Historical Notice.¹—The oldest piece of zinc extant is an idol found in a prehistoric Dacian settlement at Dordosch, Transylvania,² which upon analysis showed Zn 87.52, Pb 11.41, Fe 1.07 per cent. Its composition resembles that of "Zinkstuhl," a lead-bearing zinc, which was collected according to Löhneys³ long before 1617 in the blast furnaces of the Lower Harz. C. A. Schlüter⁴ gives details of the manner of collecting the "zinkstuhl;" B. Kerl⁵ states in the middle of the seventeenth century the word zinc is mentioned in the reports of the Lower Harz. At the works of Oker, Lower Harz, lead-bearing zinc used to be collected for many years in a pocket placed above the tap-hole of the rectangular blast furnace which received blast from a tuyere at the back. Charcoal was fed toward

¹ Fuchs, G. F. C., "Geschichte des Zinks, etc.," Erfurt, 1788.

Kopp, H., "Geschichte der Chemie," Vieweg, Brunswick, 1847, IV, 113.

Zippe, "Geschichte der Metalle," Braumüller, Vienna, 1857, 235.

Percy, J., "Metallurgy," Murray, London, 1861, 518.

Jagnaux, R., "Histoire de la chimie," Baudry, Paris, 1891, II, 207.

Seamon, W. H., "Notes on the History of Zinc," *Bull. Mo. Min. Club*, 1895, 1, 53.

Neumann, B., "Die Metalle, Geschichte, Vorkommen u. Gewinnung, etc.," Knapp, Halle, 1904, 284.

Agricola, G., Hoover, H. C. and L. H., "De re metallica," *The Mining Magazine*, London, 1912, 408-412.

Hommel, "The Origin of Zinc Smelting," *Eng. Min. J.*, 1912, XCIII, 1184.

Ingalls, "Historic Note on Zinc Smelting," *Eng. Min. J.*, 1913, XCVI, 741.

² Helm, *Verh. Berlin anthropol. Gesellschaft*, 1895, 619; *Oest. Zt. Berg. u. Hüttenw.*, 1897, XLV, 109.

³ Bergman, T., transl. by Cullen, E., "Physical and Chemical Essays," Murray, London, 1784, II, 313.

⁴ "Gründlicher Unterricht von Hüttenwerken," Meyer, Brunswick, 1738, 224.

⁵ "Die Rammelsberger Hüttenprocesse am Communion Unterharze," Grosse, Clausthal, 1861, 35.

the front and ore-charge toward the back; the zinc was condensed in the porous charcoal and collected in the pocket.¹ This method was given up in the middle of the nineteenth century when coke replaced charcoal, and charges were fed in horizontal layers.

It is generally held that the Ancients were unacquainted with zinc. There have been found, however, in the ruins of Cameros, destroyed 500 B.C., two bracelets filled with zinc; and in the ruins of Pompeii, destroyed 79 A.D., the front of a fountain, the upper part of which is covered with zinc.² The Pompeian find³ is questioned by Hofmann,⁴ as a search for the fountain in the museum of Naples has been unsuccessful.

There is nothing known about the sources of this zinc.

The Romans, as early as 200 B.C., were well acquainted with brass, but not the Greeks.⁵ Brass was prepared about the time of Augustus, 20 B.C. to 14 A.D., by a slow reducing fusion in a crucible of zincky wall accretions (cadmia) or oxide zinc ore and fragments of copper. In the operation, the zinc oxide was first reduced to metal, the zinc vapor permeated the copper; then the temperature was raised to fuse the charge. Brass was used for ornaments, coins,⁶ and other purposes.

In Asia zinc was produced much earlier than in Europe. This is shown by Kazwini, called the Pliny of the Orient, who died 630 A.D.⁷ He states that the Chinese knew how to render the metal malleable and used it for making small coins and mirrors; also that it was produced from *tutia* (Arabic) for which the Persian word is *kar-tsini* (Chinese iron), a possible origin of the word zinc. *Tutia* is the name for dust collected in the roasting of zinc-bearing sulphide ores.

¹ Details, see Kerl, *op. cit.*

² Jagnaux, *op. cit.*, II, 208.

³ Leger, A., "Les travaux publiés, etc. aux temps des Romains," Dejeu, Paris, 1875, 721.

⁴ *Berg. Hüttenm. Z.*, 1882, XLI, 528.

⁵ v. Bibra, "Die Bronzen u. Kupferlegierungen der alten u. ältesten Völker," Erlangen, 1869, 17 and 91.

Frantz, *Berg. Hüttenm. Z.*, 1881, XL, 231, 251, 337, 377, 387, 542.

Hofmann, *op. cit.*, 1882, XLI, 479, 491, 503, 515, 527.

Reyer, *op. cit.*, 1883, XLII, 59.

Gowland, *J. Inst. Met.*, 1912, VII, 23.

⁶ Lists of analyses, see Hofmann, *op. cit.*, p. 505, and Gowland, *op. cit.*, p. 45.

⁷ "Chrestomatie arabe" by Sacy, vol. 3, p. 439; through Schweigger, *Jahrbuch der Chemie u. Physik*, 1821, XXXI, 357.

In Europe the word zinc is first used by Basilius Valentinus fifteenth century, in his book, "Currus Triumphalis Antimonii,"¹ but he appears not to have been acquainted with any of its properties. The case differs with Paracelsus (sixteenth century) who in his "Heremetic and Alchemical Writings," translated by A. E. Waite, Elliott & Co., London, 1894, names the metal several times² and discusses some of its properties.³ The medieval metallurgist Agricola⁴ was not acquainted with the metal.

In 1620⁵ the Dutch captured a Portuguese vessel with a cargo of zinc from the East Indies which was sold as *speautre* or *spialter*; Boyle latinized it by calling it *speltrum*, from which comes spelter, the industrial term for zinc. Indian tin is mentioned by Boyle in "Experimenta de flammae ponderabilitate."⁶ In 1745⁷ a ship of the East India Co. coming from Canton, China, was wrecked near Gothenburg, Sweden, which had blocks of zinc on board; this contained Zn 98.990, Fe 0.765, Sb 0.245 per cent; Cu, Ni, Ag, As and Pb were absent, showing that it was from very pure ore. It appears then that zinc was imported at this period from East India or China to Europe.

According to Bergman⁸ knowledge of the art of smelting zinc ore was brought a few years previous to 1740 by Dr. Isaac Lawson from China to England where the first smeltery was erected by Champion in the brass works near Bristol in 1743. Zinc smelting continued there for about one hundred years, and was then transferred to Swansea which is the present zinc-smelting center of the United Kingdom. The process was kept secret until toward the end of the century, when Johann Richberg visited England, learned the art, returned to Upper Silesia in 1798 or 1799, and started operations at the glass works of Wessola, near Myslowitz. Upper Silesia is one of the important centers of the zinc industry of Germany, the

¹ In the abridged version "The Triumphal Chariot of Antimony" transl. by A. E. Waite, Elliott & Co., London, 1893, the passage (p. 77) has been abbreviated, leaving out the word "zinken."

² Vol. II, pp. 136, 248, 254.

³ P. 254.

⁴ *Op. cit.*, pp. 408-412.

⁵ Beckmann, J., "History of Inventions," transl. from the German of 1791 by Johnston, W., Crosby, London, 1814, III, 91.

Watson, R., "Chemical Essays," T. Evans, London, 1789, IV, 2.

⁶ William Godbid, for Moses Pitt, London, 1673, p. 15.

⁷ Hommel, *Eng. Min. J.*, 1912, XCIII, 1185.

⁸ *Op. cit.*, p. 314.

other lies on the border of Belgium. In Belgium zinc smelting was begun by the Abbé Dony in 1806 at Moresnet (Liège) near the mine of Vieille Montagne, the ores of which had been used since 1425 for making brass. The zinc industry of Belgium is centered at Liège.

Since 1820 the zinc industry has been well established in Europe. Germany and Belgium are the leading zinc centers; the others are Austria, France, Great Britain, Holland, and Poland (see Table 1).

So far only oxides of zinc were used as ore. In 1758 John Champion was granted a patent for making zinc from blende, by roasting the ore, mixing the roasted ore with charcoal, and smelting the mixture. The use of blende became more general only in the middle of the nineteenth century and forms today the principal ore.

In the United States¹ the first zinc was produced in 1835-36 by John Hitz in the arsenal of Washington, D. C., with zincite. In 1850 the New Jersey Zinc Co. erected a Belgian zinc furnace at Newark, N. J., using oxide ore from New Jersey, it failed, as the franklinite corroded the retorts; in 1856 the Lehigh Zinc and Iron Co. built at Friedensville, Pa., a Silesian furnace with a similar result, but in 1859 it worked successfully a Belgian furnace with 45 retorts; in 1860 J. Wharton erected in South Bethlehem, Pa., a plant with 16 Belgian furnaces, each with 72 retorts. Thus the Lehigh Valley was the cradle of the American zinc industry. In the West experiments with zinc smelting were carried on by A. M. Anderson at Potosi, Mo., as early as 1855; a large furnace was erected in 1856, but was not operated; in 1857 a small plant was built at Calamine, Ark., but was not successful. The first successful smeltery was erected by F. W. Matthiessen and E. C. Hegeler at La Salle, Ill., in 1853; it was finished in 1860, and has been a large producer ever since. Then followed several works at or near St. Louis² and Mineral Point, Wis.; later in the seventies came the works of the Chicago Zinc and Mining Co. at Weir City, and Pittsburgh, Kan. The year 1860, with the plant of the Lehigh Zinc Co. at South Bethlehem, Pa., and the Matthiessen and Hegeler plant at La Salle, Ill., marks the

¹ "American Encyclopedia," Ripley, G. A., Dana, C. A., Appleton, New York, 1873-76.

Winslow, A., Missouri Geological Survey, vol. vi (Lead and Zinc), Jefferson City, Mo., 1894, Part I, pp. 12-14; also *Eng. Min. J.*, 1894, LVIII, 488; 1895, LIX, 51.

Ingalls, W. R., "Lead and Zinc in the United States," McGraw-Hill Book Co., Inc., New York, 1908, Part II.

Sieenthal, C. E., *Bull. Am. Zinc Inst.*, July, 1919, vol. II, No. 7, p. 86.

² Meister, *Tr. A. I. M. E.*, 1905, xxxv, 734.

beginning of American zinc industry. The works of the Illinois Zinc Co. at Peru, Ill., were started in 1870. At present the leading smelteries are found in Oklahoma, Illinois, Pennsylvania, Kansas and Arkansas.

The manufacture of zinc oxide from ore was started by S. Wetherill in 1855 in the Passaic zinc works at Jersey City, N. J. (see §137).

In 1805, Hobson and Sylvester of Sheffield discovered that the brittle zinc could be rolled into sheets at a temperature ranging from 100° to 150°C. The first rolling mill was built by Abbé Dony at Liège in 1812; the first sheet zinc in the United States was made in Philadelphia in 1857 (see §21).

It is usually held that the process of galvanizing (§15) was invented by H. W. Crawford in 1837; Lang,¹ however, states that as early as 1741 Malouin coated iron with zinc, and shows that the patent of Sorel of 1836 contains all the essentials of the process.

2. **Statistics.**—The world's production of zinc in 1913 and 1919 is given in Table 1, and that of the United States in 1917 to 1920 in Table 2. Table 1 shows in 1913 the United States was the leading producer furnishing 31.4 per cent of the world's output, it was closely

TABLE 1.—WORLD'S PRODUCTION OF ZINC IN 1913 AND 1919²

	1913	1919
Belgium.....	193,645	15,607
Germany { Silesia.....	167,507	35,422
{ Rhineland and other parts.....	109,544	11,146
France.....	63,412	18,000
United Kingdom.....	31,290	21,543
United Kingdom refiners.....	27,008	7,822
Holland.....	23,958	<i>Nil.</i>
Austria.....	20,736	4,000
Poland.....	15,708	2,500
Spain.....	8,917	1,500
Norway.....	9,600	3,386
European total.....	671,325	120,926
Australia.....	3,666	2,594
United States.....	308,549	400,800
Japan.....		22,000
Canada.....		11,160
World's total.....	983,540	566,480

¹ *Rev. Mét.*, 1912, IX, 21.

² *Min. Ind.*, 1919, XXVIII, 743.

TABLE 2.—ZINC PRODUCED IN THE UNITED STATES, 1917-1920, IN SHORT TONS

	1917	1918	1919	1920
Arkansas.....	25,660	26,753	31,437	31,481
Illinois.....	172,489	141,844	(a) 118,340	(a) 108,851
Kansas.....	76,048	29,149	43,942	41,044
Oklahoma.....	204,394	139,066	121,988	110,931
Pennsylvania.....	86,995	77,342	67,521	74,234
Other States.....	78,778	64,857	55,459	45,641
Electrolytic.....	25,209	38,916	27,056	51,626
Total primary.....	669,573	517,927	465,743	463,808
From domestic ore.....	584,597	492,405	452,272	450,476
From foreign ore:				
Australia.....	26,140	1,780	630	2,235
Canada.....	6,787	8,700	4,007	1,583
Chile.....		886	751	536
Italy.....	2,951	113		
Mexico.....	40,360	14,043	8,083	8,978
Spain.....	8,738			
Total foreign.....	84,976	25,522	13,471	13,332
Total primary.....	669,573	517,927	465,743	463,808
Redistilled secondary.....	16,835	9,918	19,748	21,371
Total.....	686,408	527,845	485,491	485,179
Grade {				
High grade.....	97,707	129,344	45,377	80,713
Intermediate.....	69,189	68,987	39,173	33,893
Brass special.....	148,749	98,584	140,917	59,811
Prime western.....	370,763	230,930	260,024	310,762
Total.....	686,408	527,845	485,491	485,179
Average selling price per pound:				
Grade {				
High grade.....	14.0 cents	11.1 cents	8.3 cents	8.4 cents
Intermediate.....	12.7 cents	10.7 cents	7.7 cents	8.3 cents
Brass special.....	9.4 cents	8.0 cents	7.2 cents	8.2 cents
Prime western.....	9.0 cents	7.9 cents	7.1 cents	8.0 cents
All grades.....	10.2 cents	9.1 cents	7.3 cents	8.1 cents
Total value of output.....	\$140,027,000	\$96,068,000	\$70,882,000	\$78,599,000

(a) Exclusive of electrolytic zinc made in Illinois.

Prepared by C. E. Siebenthal, March 3, 1921.

followed by Germany, third in order came Belgium; the three countries furnishing nearly 80 per cent. The United States treats mainly domestic ores; Germany has important zinc mines in Silesia, the Rhenish provinces smelt mainly imported ores; the Belgian mines having been exhausted the smelting industry depending entirely on foreign ores.

Beside metallic zinc there is produced in the United States zinc oxide direct from ore. The amount for 1919 was 117,639 tons with a market value of \$175.04 per ton.¹

3. Bibliography.—All treatises dealing with non-ferrous metallurgy have a chapter on the metallurgy of zinc. The subject is discussed by Percy (1867), Kerl (1881), Balling (1885), Schnabel-Louis (1905), Hildebrandt (1906), Prost (1912), and Gowland (1918). The accompanying list contains the four books devoted to zinc alone; there is added a bibliography covering the periodical literature.

Ingalls, W. R., "The Metallurgy of Zinc and Cadmium," McGraw-Hill Book Co., Inc., New York, 1903.

Lodin, A., "Métallurgie du Zinc," Dunod, Paris, 1905.

Liebig, R. G. M., "Zinc und Cadmium," Spamer, Leipsic, 1913.

Smith, E. A., "The Zinc Industry," Longmans, Green & Co., London, 1918.

Wheeler, H. L., "Bibliography on the Roasting, Leaching, Smelting, and the Electrometallurgy of Zinc," School of Mines and Metallurgy, University of Missouri, Rolla, Mo., *Bulletin*, February, 1918.

¹ *Min. Ind.*, 1919, XXVIII, 729.

CHAPTER II

PROPERTIES OF ZINC

4. Physical Properties.—Specimens of native zinc have been found in Australia and Alabama. The metal has a bluish-white color and a metallic luster on a new fracture. The specific gravity of zinc cast near its melting point is 7.10 to 7.16 when cooled slowly, and 7.04 to 7.14 when cooled quickly, the difference being probably due to the formation of larger or smaller crystals; rolled zinc has a specific gravity of 7.19, molten zinc one of 6.48; 1 cu. ft. of cast zinc weighs 439 to 447 lb.; of wrought, 449 lb.; of liquid, 404 lb. Zinc ordinarily forms hexagonal crystals; in alloys isometric



FIG. 1.—Dendrite on surface of cast zinc.

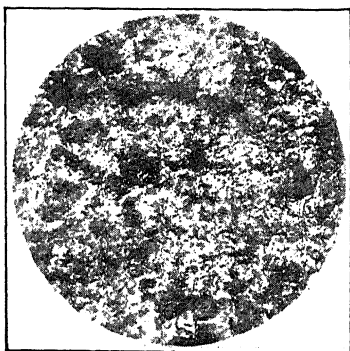


FIG. 2.—Etched surface of slowly cooled zinc.

crystals have been found. Figure 1¹ shows a dendrite on the surface of metal cast on stone; Fig. 2² represents the etched surface of slowly cooled metal, it shows comparatively large grains with a needle structure similar to that of martensite. The fracture is coarsely crystalline when poured at a temperature near to redness, granular when poured not much above its melting point; the metal being cooled slowly in both cases. Recent research has shown that zinc is

¹ Campbell, 6th Report, Appendix 4, Alloys Research Committee, 1901.

² Timoeff, *Rev. éMét*, 1914, XI, 128.

polymorphous.¹ Transformations have been noted at 340° to 350°C. by Le Chatelier² and by Benedicks-Apri³ at 170°, 270° and 350°C. These transformations were attributed later by the authors⁴ to the presence of Cd and perhaps of Pb, but Cohen-Helderman⁵ maintain that the original figures are correct and note⁶ an additional change below 100°C. Jaenecke⁷ found a transformation between 104° and 220°, and Laschtschenko⁸ verified by a different method of research the figure of Le Chatelier. It is believed that there exist three modifications of zinc; α -zinc from (?) to 170°C., β -zinc from 170° to 330°, and γ -zinc from 330° to 419.4°C. Bingham⁹ concludes from a study of the electric resistance, electrolytic potential, specific gravity, hardness, and mechanical properties, at different temperatures, that there exist three allotropic forms of zinc, and that the limits of α , β , and γ zinc given are only approximations. The metal is soft having a scratch-hardness of 2.5 Mohs scale, or 6.0 Turner Sclerometer, 7.0 Shore scleroscope, 7.5 $\frac{\text{Brinell}}{6}$ ¹⁰; it is harder than tin and softer than annealed copper. It is difficult to file, is slightly sonorous; at 160°C. it emits a crackling sound when bent, similar to the cry of tin, but weaker. At ordinary temperature it is brittle, being easily broken by striking with a hammer; at 100° to 150°C. it becomes malleable so that it can be rolled into sheets, and ductile to be drawn into wire.¹¹ It is less malleable than lead and more than iron, less ductile than copper and more than tin. Fine-grained zinc is easier to roll and draw than coarse; in addition to temperature the malleability and ductility depend largely on purity.¹²

Uniform heating to 150° is favored by the use of a bath of heavy

¹ Benedicks, *Metallurgie*, 1910, VII, 531.

² *Compt. rend.*, 1890, CXI, 414, 454; "Contributions à l'Étude des Alliages," Chamerot-Renouard, Paris, 1901, 416.

³ *Zt. anorg. Chemie*, 1914, LXXXVIII, 237.

⁴ *Op. cit.*, 1914, XC, 153.

⁵ *Zt. phys. Chem.*, 1915, LXXIX, 742.

⁶ *Op. cit.*, 1914, LXXXVII, 409.

⁷ *Op. cit.*, 1915, XC, 321.

⁸ *J. Russian Physico-Chem. Soc.*, 1913, X, 424, through *J. Inst. Met.*, 1913, X, 424.

⁹ *J. Inst. Metals*, 1920, XXIV, 333.

¹⁰ Turner, *J. I. & St. I.*, 1909, I, 434.

¹¹ Haines, *Proc. Roy. Soc.*, 1911, LXXXV, 526.

¹² Mathewson-Travin-Finkeldey, *Tr. A. I. M. E.*, 1920, LXIV, 305.

oil with high flash-point.¹ At 200°C. zinc becomes so brittle that it can be pulverized. The tensile strength of cast zinc varies from 8,000 with coarse to 14,000 lb. per square inch with fine grain metal; of drawn zinc from 22,000 to 30,000 and even 40,000 lb. per square inch across the grain.² The modulus of rupture of cast metal varies from 8,000 to 22,000 lb. per square inch with deflections of from 0.09 to 0.44 in. in a span of 12 in. The loads necessary to compress cylinders (1 in. in diameter and 2.6 in. long) 10 and 20 per cent are in pounds per square inch.

	10 PER CENT	20 PER CENT
High grade.....	16,500	23,095
Intermediate.....	16,065	23,095
Brass special.....	18,310	26,000
Prime western.....	20,570	28,620

Resistance to compression increases with amount of impurity. Particles of zinc can be united under a pressure of 76,000 lb. per square inch.³ The melting point is 419.4°C.;⁴ the boiling point is 920°C.;⁵ *in vacuo* zinc begins to sublime at 184°.⁶ Johnson⁷ has shown that the rise of boiling point above normal (920°C. at 760 mm.) is 6.1°C. for 1 lb. pressure; this makes it 1,080°C. for 25 lb., 1,350° for 75 lb.; the curve is nearly a straight line. The author⁸ has given vapor tension curves of zinc and related metals. The vapor is monatomic. The mean specific heat⁹ of the metal between 0° and t° is $0.0906 + 0.000044t$. The quantity of heat to bring from 0° to melting point 45.2 cal.; the latent heat of fusion is 22.6 cal., hence, the quantity of heat in molten metal at melting point is $45.2 + 22.6 = 67.8$ cal. The specific heat of liquid metal is 0.179 (Glaser). The quantity of heat in metal at boiling point (930°C.)

¹ *Metal Industry*, 1904, II, 21; *Eng. Min. J.*, 1904, LXVII, 474.

² Moore, *Univ. Ill.*, 1911, IX, Bull. 9.

Stone, *Tr. Am. Inst. Met.*, 1914, VIII, 183.

³ Spring, *Ber. deutsch. chem. Gesellsch.*, 1882, XV, 595; *Bull. soc. chim.*, 1883, XI, 250.

⁴ Holborn, Henning, *Ann. Phys.*, 1911, XXXV, 761.

⁵ Berthelot, *Compt. rend.*, 1900, CXXXI, 1900.

⁶ Friedrich, "Vacuum-temperature Curve," *Stahl u. Eisen*, 1911, XXXI, 2,044.

⁷ *Min. Met. Soc. America*, 1915, Bull. 90, p. 247; *Met. Chem. Eng.*, 1916, XIV, 105.

⁸ *Met. Chem. Eng.*, 1917, XVI, 485.

⁹ Richards, J. W., "Metallurgical Calculations," McGraw-Hill Book Co., Inc., New York, 1918, 87.

is 159 cal., the latent heat of vaporization is 446 cal. (calculated), hence, the quantity of heat in vapor at 930°C. is $459 + 446 = 605$ cal. The specific heat of vapor is 0.225 per m.³ and 0.077 per kilogram. The vapor tension, p , liquid is $\log p = -\frac{6.365}{T \text{ absolute}}$ + 8.17; at melting point = 9.3×10^2 mm. Hg; solid, $\log p = -\frac{6.685}{T \text{ absolute}}$ + 8.63; at 0°C. = 1.03×10^{-16} mm. Hg. The thermal conductivity per cm.³ per degree per second is 0.26 cal.

The linear expansion coefficient at 0° to 100°C. is 0.000029, but sheet zinc which expands during the summer does not contract again in winter to its original size; a new sheet does not assume its original length as well as does an old one.¹ The cubical coefficient of expansion at 0° to 100°C. is 0.00089. The specific resistance at 0°C. is 5.56–6.04 microhms per cm.³; for solid zinc at melting it is 18.16 microhms, and for liquid zinc at melting point, 36.00.² Zinc is diamagnetic.

5. Chemical Properties.—The atomic weight is 65.38. Dry air or air free from CO₂ does not attack zinc at ordinary temperature, moist air oxidizes the surface forming a grayish coating with a composition approximating ZnCO₃ · 3Zn(OH)₂³ which protects the metal from further oxidation.⁴ Commercial zinc⁵ exposed for 5 years to the air, lost 92.4 to 102 gr. per square meter; increase of Cd, Pb, Sn, As + Sb had no effect; Sb favored corrosion; Cu protected the zinc as long as its amount did not exceed 0.01 per cent, the same was the case with As + Sb to the extent of 0.009 per cent. At a red heat water is decomposed by zinc forming crystalline ZnO. Heated in the presence of air just above its melting point zinc becomes coated with a gray film consisting of oxide and finely divided metal; at 505°C. it burns with a bluish-white flame to amorphous ZnO, and continues to burn when once ignited, part of the oxide passes off into air (*lana philosophica*), part remains on the bath of metal. The gas CO₂ begins to oxidize zinc at 300°C. (see §25). Heating with KNO₃ or KClO₃ quickly oxidizes Zn to ZnO, with As₂O₅ or As₂O₃ forms arsenite or arsenide of zinc, with K(Na)₂ SO₄

¹ Vosmaer, *Mét. Chem. Eng.*, 1915, XIII, 954.

² "Handbook Electrical Engineers," McGraw-Hill Book Co., Inc., New York, 1915, p. 268.

³ *Min. Ind.*, 1903, XII, 364.

⁴ Bauer-Wetzel, *Zl. Metallkunde*, 1919, X, 1

⁵ Prost, *Rev. Un. Min.*, 1920, VI, 353.

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forms ZnO and Zn_2SO_4 . Its behavior with S, Se, Te, Cl, Br, I, P, As, P, C, Si, is taken up in §7 and following.

Zinc is readily soluble in dilute H_2SO_4 and HCl with evolution of H_2 , less quickly in solutions of alkali; with HNO_3 there is formed N_2O_3 , a little NO , and often considerable N_2O ; concentrated H_2SO_4 and H_2SO_3 are reduced to H_2S . It is electropositive to all heavy metals and precipitates these from their solutions, Mn, Fe and Ni forming an exception.

ZINC OF COMMERCE OR SPELTER. ITS IMPURITIES
AND THEIR EFFECTS¹

6. Grades of Spelter.—The primary spelter of smelting varies as regards purity.² The impurities are all harmful in the industrial uses of the metal. Their amount is under 3 per cent; Horsehead, Bertha and Tennessee brands, as well as electrolytic spelter contain over 99 per cent Zn.

Spelter is commonly cast in the form of plates, 7 by 24 by 1 in., weighing 40 to 45 lb., or 11 by 18 by 1 in., weighing 45 to 55 lb., or similar sizes and weights.

In the United States four commercial grades of primary metal are distinguished: High grade, intermediate, brass special, and prime western (see Table 2). They are graded according to the amounts of Cd, Pb, and Fe they contain and the presence or absence of Al as seen in Table 5 by Siebenthal³ which gives the specifications of the leading associations of the country. They show the lowest permissible percentages of Zn, the maxima of the usual impurities Cd, Pb, and Fe, and the totals of these impurities. It will be noted that the requirements for purity have been lowered by the Ordnance Department of the United States Army and the New York Metal Exchange on account of difficulty of obtaining the necessary amounts of metal. High grade is for brass that is spun or drawn; intermediate, for brass which does not require high ductility; brass special, for better grades which need not have much ductility; prime western, for galvanizing, brass castings. The effects of the impurities and the limits they impose upon the uses are given in §7 and following.

Beside primary spelter there is sold in the market secondary metal with 3 to 5 per cent Fe and 2 to 3 per cent Pb, resulting from the melting of scrap, drosses, sometimes called hard spelter, which is

¹ Stone, *Am. Inst. Met.*, 1914, VIII, 174; *Min. Sc. Press*, 1914, CIX, 754.
Ingalls, *Eng. Min. J.*, 1915, XCIX, 292.

Stone-Bassett-Price, *Foundry*, 1916, XLIV, 326.

Mathewson-Trewin-Finkeldey, *Tr. A. I. M. E.*, 1920, LXIV, 305.

² Sampling, *Eng. Min. J.*, 1916, CII, 108, 358.

³ *Chem. Met. Eng.*, 1918, XIX, 504.

TABLE 5.—SPELTER SPECIFICATIONS

	Zn	Cd, maxi- mum	Fe, maxi- mum	Pb, maxi- mum	Cd, Fe, Pb, maxi- mum sum	Al, maxi- mum	Other ele- ments
A. High grade							
1		0.05	0.03	0.07	0.10	0	
2		0.07	0.03	0.07	0.10	0	
3	99.85	0.05	0.03	0.07	0.10	0	0
4	99.50	0.50	0.03	0.10	0.50	0	0
B. Intermediate							
1		0.50	0.03	0.20	0.50	0	
2		0.50	0.03	0.20	0.50		
3	99.35	0.50	0.03	0.20	0.50	0	tr.
4	99.35	0.50	0.03	0.25	0.65	0	tr.
C. Brass special							
1		0.75	0.04	0.75	1.20	0	
2		0.50	0.03	0.60	1.00	0	
2		0.75	0.04	0.80	1.25	0	
3	98.00	0.75	0.08	1.00	1.50	tr.	tr.
4	98.00	0.75	0.08	1.00	1.50	tr.	tr.
5	98.60	0.75	0.04	0.75	1.20	tr.	tr.
D. Prime western							
1			0.08	1.50			
2			0.08	1.60			
5	98.00	0.75	0.08	1.50	2.00	tr.	tr.
6			0.08	2.00			

1. Am. Soc. Test. Mat. *Proc.*, vol. XI, pp. 147-149, 1911; adopted Aug. 21, 1911.

2. Am. Soc. Test. Mat. *Proc.*, vol. XVI, pp. 583-589, 1917; vol. XVII, pp. 180-181, 1917.

3. Navy Department Specifications, 47Zld, June 1, 1917.

4. U. S. Army, Ordnance Department Specifications, Revised March 7, 1918.

5. Navy Department Specifications, 47Zlb, Nov. 1, 1913.

6. New York Metal Exchange Specifications; *American Metal Market*, Aug. 31, 1916.

likely to be impure from admixture of other metals. Thus in 1918¹ the output of secondary zinc amounted to 23 per cent of the production of primary metal. Some secondary metal is of excellent quality. Redistillation of low-grade spelter is taken up in §113.

¹ Dunlop, "Min. Resources U. S.," 1918, I, 596.

Analyses of spelter from some European countries and the United States are given in Tables 6 and 6a.

In Table 6a some rare elements present in the American samples have been identified by spectrograph; most these samples contained traces of Sn and Ag. In the residues of some American chemical works there have been found gallium (Ga), indium (In), and germanium (Ge);¹ the metals In, Tl, and Ge have been found in samples of blende from Cornwall² and Rhenish Prussia.³

TABLE 6.—CHEMICAL ANALYSES OF EUROPEAN SPELTER

	Vieille Montagne, Belgium	Stolberg- Münster- busch, Rhenish Prussia	Georg Works, Silesia	Giese Works, Silesia	Paul Works, Silesia
Zn.....	99.411	98.8660	98.4973	98.7832	98.930
Pb.....	0.540	1.1165	1.4483	1.1921	1.000
Cd.....	tr.	0.0083	0.0245		0.018
Fe.....	0.049	0.0067	0.0280	0.0238	0.030
Cu.....		0.0005	0.0002	0.0002	
Ag.....			0.0017	0.0007	
As.....		0.0015	tr.		0.012
Sb.....		0.0005		tr.	
Bi.....				tr.	
S.....			tr.	tr.	
Tl.....					0.010

Metallurgie, 1910, VII, 201.

Steger, "Verdichtung der Metaldämpfe in Hüttenwerken," Enke, Stuttgart, 1896, p. 78.

7. Impurities and Their Effects.⁴—The specifications given in §6 show that in practice Cd, Pb, and Fe are the only foreign metals considered in determining the character of commercial zinc, as other metals are present in quantities too small to have any decided effect upon the physical properties. These three metals and others found in impure spelter are taken up in §§8 to 12.

¹ *Eng. Min. J.*, 1916, CI, 720, CII, 335; *J. Ind. Eng. Chem.*, 1916, VIII, 225, *J. Am. Chem. Soc.*, 1919, XLI, 947.

² *American Chemist*, 1877, p. 339; *Berg. Hüttenm. Z.*, 1877, XXVI, 215.

³ *Berichte deutsch. chem. Gesellsch.*, 1879, XII, 276, 382; *Berg. Hüttenm. Z.*, 1879, XXVIII, 206; *Chem. Z.*, 1880, IV, 443.

⁴ Arnemann, *Metallurgie*, 1910, VII, 201.

Rigg-Morse, *Tr. Am. Inst. Met.* 1915, IX, 26.

TABLE 6a.—CHEMICAL ANALYSES OF THREE GRADES OF AMERICAN SPELTER

	Zn	Impu- rities	Pb	Fe	Cd	Cu	Bi	Ga	In	Tl	Ge	Sb
Intermediate	99.889	0.111	0.035	0.004	0.072							
	99.873	0.127	0.043	0.011	0.073		*			*		
	99.870	0.130	0.051	0.008	0.071							
	99.853	0.147	0.020	0.005	0.122	*						
	99.797	0.203	0.189	0.014	0.000		*				*	*
	99.748	0.252	0.239	0.013	0.000		*		*	*		
	99.745	0.255	0.037	0.018	0.200							
	99.726	0.274	0.013	0.017	0.244							
	99.719	0.281	0.091	0.006	0.184		*					
	99.700	0.300	0.151	0.029	0.120		*		*			*
	99.690	0.310	0.184	0.014	0.112							
	99.645	0.355	0.144	0.010	0.201		*		*			
	99.634	0.366	0.065	0.017	0.284		*	*	*			
	99.630	0.370	0.172	0.004	0.194				*			*
	99.621	0.379	0.361	0.018	0.000		*		*			*
	99.578	0.422	0.256	0.033	0.133		*					*
	99.545	0.455	0.150	0.007	0.298				*			
	99.510	0.490	0.448	0.008	0.034							
Brass special	99.377	0.623	0.007	0.001	0.615					*		*
	99.352	0.648	0.415	0.010	0.223					*		
	99.345	0.655	0.478	0.013	0.164		*		*			
	99.299	0.701	0.155	0.012	0.534							
	99.295	0.705	0.475	0.015	0.215					*		
	99.235	0.765	0.402	0.017	0.346			*	*			
	99.215	0.785	0.526	0.031	0.228		*					
	99.213	0.787	0.434	0.011	0.342							
	99.137	0.863	0.512	0.024	0.327		*		*	*		
	99.091	0.909	0.581	0.025	0.303	0.038	*		*	*		
	99.068	0.932	0.588	0.007	0.337				*			
	99.004	0.996	0.747	0.024	0.225		*		*			
	98.991	1.009	0.818	0.019	0.172				*	*		
	98.967	1.033	0.802	0.027	0.204		*		*	*		
	98.961	1.039	0.222	0.008	0.809		*		*			
Prime western	98.915	1.085	0.858	0.012	0.215		*		*			
	98.860	1.140	0.972	0.025	0.143		*					
	98.789	1.211	0.812	0.021	0.378		*		*			*
	98.751	1.249	0.816	0.052	0.381		*		*	*		
	98.727	1.273	0.940	0.037	0.296	0.002	*	*	*	*	*	
	98.705	1.295	0.919	0.037	0.339		*		*	*		
	98.686	1.314	1.043	0.046	0.225		*		*	*	*	
	98.560	1.440	1.277	0.034	0.129		*	*	*	*	*	*
	98.553	1.447	1.254	0.040	0.153				*	*	*	*
	98.501	1.499	1.251	0.023	0.225	0.039	*		*	*	*	*
	98.447	1.553	1.412	0.069	0.072	0.003	*		*	*	*	*
	98.442	1.558	1.150	0.075	0.333				*	*	*	*
	98.418	1.582	1.406	0.054	0.122				*	*	*	*
	98.376	1.624	1.433	0.079	0.112	0.009	0.032		*	*	*	*
	98.221	1.779	0.626	0.039	1.114	0.004		*		*	*	*
	97.789	2.211	1.934	0.134	0.143		*		*	*		*

* = Identified by Spectograph.

8. Cadmium.¹—Zinc and cadmium when fluid are miscible in all proportions, and form no solid solutions. This is seen from the freezing-point curve, Fig. 3,² which shows an eutectic with 82.6 per cent Cd freezing at 270°C., and the insolubility in the solid state. The effect of Cd³ is to harden the spelter and make it more brittle, especially hot-short; compression tests by Stone⁴ bring this out clearly.

As little as 0.05 per cent. Cd fails to furnish thin flush (ornamental) castings;⁵ in galvanizing, zinc practically free from Cd is demanded, as the coatings crack and peel off, when wire is sharply bent. In rolling,⁶ 0.25 per cent is permissible; with 0.30 per cent the metal

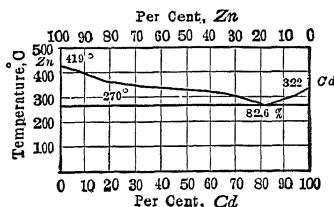


FIG. 3.—Alloy series Zn-Cd.

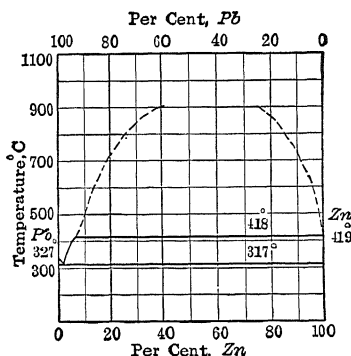


FIG. 4.—Alloy series Zn-Pb.

cracks; 0.5 per cent makes rolling impossible. In brass,⁷ it weakens the alloy and makes it likely to crack; however, in using Cd-bearing spelter the melter uses a high temperature and a long duration of the melt, and thus volatilizes practically all the cadmium. The electric conductivity⁸ is proportional to the atomic volume.

9. Lead.—The constitution of this alloy series has been investigated by Heycock-Neville,⁹ and Arnemann,¹⁰ and the mutual solubility by Spring-Romanoff¹¹ and Rössler-Edelmann.¹² The

¹ Ingalls, *Eng. Min. J.*, 1905, LXXIX, 697, 1916, CII, 561.

² Heycock-Neville, *J. Chem. Soc.*, 1897, CXXI, 383.

Hindrichs, *Zt. anorg. Chemie.*, 1907, LV, 417.

³ *Tr. Am. Inst. Met.*, 1914, VIII, 185.

⁴ *Eng. Min. J.*, 1916, CII, 909.

⁵ Rigg-Morse, *Tr. Am. Inst. Met.*, 1915, IX, 26.

⁶ Prost, *Rev. Un. Min.*, 1913, II, 45; *Metall und Erz.*, 193, X, 728.

⁷ Ingalls, *Eng. Min. J.*, 1916, CII, 561.

Stone, *ibid.*, 909.

⁸ Glasunow-Matweeu, *Int. Zt. Metallographie*, 1914, V, 113.

⁹ *J. Chem. Soc.*, 1897, LXXI, 394.

¹⁰ *Metallurgie*, 1910, VII, 201.

¹¹ *Zt. anorg. Chemie*, 1897, XIII, 29.

¹² *Berg. Hüttenm. Z.*, 1890, XLIX, 245.

freezing-point curve, Fig. 4, shows that the two metals form one eutectic with 98.5 per cent Pb freezing at $317^{\circ}\text{C}.$, and at about $950^{\circ}\text{C}.$, a homogeneous solution. The saturation-point curve, traced to $900^{\circ}\text{C}.$, shows at this temperature a separation into saturated and unsaturated solutions; with the fall of temperature the mutual solubility decreases to the melting point of zinc, $419^{\circ}\text{C}.$, which is lowered 1° by zinc taking up 0.5 per cent Pb. At 418° there exist conjugate solutions. Upon further cooling, an interchange takes place in the liquid metal until its Pb-content has increased to 96.6 per cent, when the temperature falls to the eutectic point of $317^{\circ}\text{C}.$

In Table 7 are given the data of Spring and Romanoff showing the solubility of lead in zinc at different temperatures, and in Table 8 similar figures of Rössler-Edelmann.

TABLE 7.—SOLUBILITY OF LEAD IN ZINC (SPRING-ROMANOFF)

Temperature, degrees Centigrade.....	419	475	514	584	650	740	800	900
Lead retained by zinc, per cent.....	1.5	2.0	3.0	5.0	7.10	10.0	14.0	25.5

TABLE 8.—SOLUBILITY OF LEAD IN ZINC (RÖSSLER-EDELMANN)

Temperature, degrees Centigrade....	400	500	600	700
Lead retained by zinc, per cent.....	1.7	2.3	3.5	5.6

The figures in Table 7 are considerably higher than those in Table 8; they are also closer to the data of the saturation-point curve. The two tables show that in purifying crude lead-bearing zinc by liquation the lead content of the liquated zinc can not be reduced to below 1.5 per cent.

The effect of lead on zinc castings is to make them brittle, 0.7 per cent becoming noticeable; in galvanizing it tends to weaken the coating and to make it liable to peel when the metal is bent; in rolling the limit of lead-content is 1.5 per cent,¹ a smaller amount, say 1 per cent, assists in rolling, as it makes the spelter softer; in

¹ Prost, *loc. cit.*

common brass (60Cu - 40Zn), 0.08 to 0.9 per cent is permissible,¹ but with 1 per cent trouble arises; in cartridge brass even 0.1 per cent is undesirable.

10. Iron.—The freezing-point curve of Vegesack² and Arnemann³ given in Fig. 5, shows two chemical compounds, FeZn_7 at 662° , and FeZn_{13} at 777°C ., as well as a solid solution of Zn with 0.7 per cent Fe. The amount found in primary spelter is usually small. Its presence is due mainly to the manner in which the smelting operation has been conducted, as it is possible to make spelter as free from Fe from ores containing 10 to 12 per cent Fe as it is from ores with 0.1 to 0.2 per cent. The presence of iron is mainly due to careless drawing of zinc from the retort by which some charge is removed with the zinc, and to poor tools. When zinc contains over 0.1 per cent Fe, the metal has a grayish appearance and shows black specks on the crystal faces of a fractured cake. The effect of iron is to increase hardness and brittleness, and thus to reduce malleability. In rolling, 0.12 per cent⁴ interferes with the work, and the hardness and brittleness of the metal increase rapidly with greater amounts.

11. Carbon and Silicon.—Small amounts of carbon are frequently found in spelter; they are considered to be a mechanical admixture, as they are readily separated by filtering the liquid metal through asbestos.⁵

Silicon is sometimes recorded in chemical analyses of spelter. According to Moissan-Siemens⁶ Zn dissolves at 600°C ., 0.06 per cent Si; at 650° , 0.15 per cent; at 730° , 0.57 per cent; at 800° , 0.92 per cent; at 850° , 1.62 per cent Si.

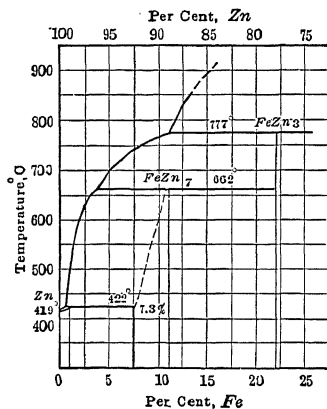


FIG. 5.—Alloy series Zn-Fe.

¹ Guillet, *Rev. Mét.*, 1906, III, 273.

Johnson, *J. Inst. Mct.*, 1912, VII, 201.

Carpenter, *op. cit.*, 1912, VIII, 63.

² *Zt. anorg. Chemie*, 1907, LII, 37.

³ *Metallurgie*, 1910, VII, 201.

⁴ Prost, *loc. cit.*

⁵ Funk, *Zt. anorg. Chemie*, 1896, II, 49.

⁶ *Compt. rend.*, 1904, CXXXVIII, 657.

12. **Other Metals.**—Metals such as Cu, As, Sb, Sn, Al are rarely found, if at all, in primary spelter; some of them are not infrequent in secondary metal. Metals like Ag,¹ Au,² Bi,³ Ca,⁴ Co,⁵ Cr,⁶ K,⁷ Mg,⁸ Mn,⁹ Na,¹⁰ Ni,¹¹ and Tl¹² are even of less interest as regards impurities in spelter.

1. **Copper.**—The freezing-point curve of Shepherd,¹³ Tafel¹⁴ and Parravano,¹⁵ given in Fig. 6, shows that a small addition of copper¹⁶ to zinc raises the melting point, and up to 2.5 per cent Cu there is

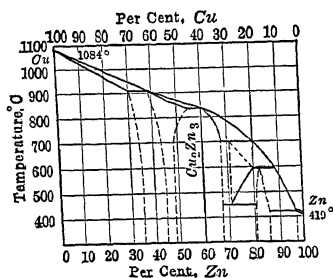


FIG. 6.—Alloy series Zn-Cu.

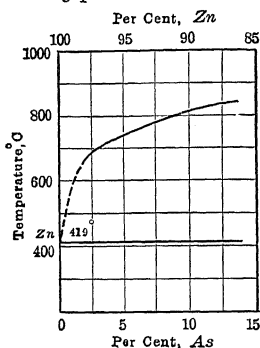


FIG. 7.—Alloy series Zn-As.

formed a solid solution η which has the color of zinc. According to Prost¹⁷ 0.06 to 0.07 per cent Cu does not interfere with the malleability excepting that a rolled sheet has ragged edges; with

¹ Carpenter-Whiteley, *Internat. Zt. Metallographie*, 1913, III, 145; *J. Inst. Met.*, 1913, IX, 214.

² Vogel, *Zt. anorg. Chemie*, 1906, XLV, 323.

³ Heycock-Neville, *J. Chem. Soc.*, 1897, LXXI, 394.

⁴ Donski, *Zt. anorg. Chemie*, 1908, LVII, 189.

⁵ Lewkonja, *op. cit.*, 1908, LIX, 321.

⁶ Hindrichs, *op. cit.*, 1908, LIX, 427.

Le Chatelier, *Bull. Soc. d'Encour.*, 1895, X, 388.

⁷ *Zt. anorg. Chemie*, 1908, LVI, 116.

⁸ *Op. cit.*, 1906, XLIX, 80.

⁹ Bornemann, *Metallurgie*, 1909, VI, 644.

Boudouard, *Rev. Mét.*, 1908, V, 787.

Gieren, *Zt. Metallkunde*, 1919, XI, 14.

¹⁰ Mathewson, *Zt. anorg. Chemie*, 1906, XLVIII, 196.

¹¹ Tafel, *Metallurgie*, 1907, IV, 784.

Voss, *Zt. anorg. Chemie*, 1908, LVII, 68.

¹² Vegesack, *op. cit.*, 1907, LII, 32.

¹³ *J. phys. Chemistry*, 1904, VIII, 421.

¹⁴ *Metallurgie*, 1908, V, 349.

¹⁵ *Gazz. Chim. Ital.*, 194, XLIV, 478.

¹⁶ Arnemann, *loc. cit.*, gives details of zinc with 1 to 10 per cent Cu.

¹⁷ *Op. cit.*

0.08 per cent the hardening effect becomes apparent, and with 0.19 per cent Cu rolling is impossible.¹

2. *Arsenic*.—According to the diagram of Friedrich and Leroux,² Fig. 7, zinc and arsenic have no affinity whatever for one another. It has a hardening effect, 0.02 per cent As is noticeable, 0.03 per cent makes zinc somewhat brittle, 0.09 per cent decidedly so; however, zinc with 0.09 per cent As can still be rolled if the necessary care is taken.³ In the presence of arsenic, boiling a cyanide precipitate in sulphuric acid requires special precautions to carry off the H_3As which is liberated.

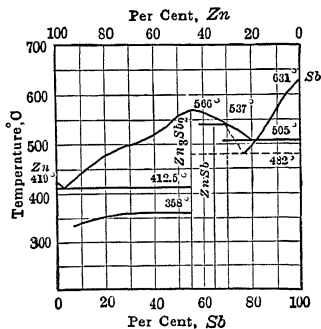


FIG. 8.—Alloy series Zn-Sb.

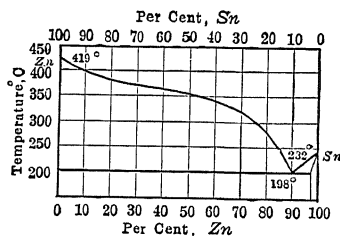


FIG. 9.—Alloy series Sn-Zn.

3. *Antimony*.—The freezing-point curve of Schemtschuschny,⁴ Fig. 8, shows at the zinc-end an eutectic with 2.5 per cent Sb freezing at 412.5°C. Its effects are less harmful than those of arsenic;⁵ zinc with 0.02 to 0.07 per cent Sb can be readily rolled, the sheet showing ragged edges and a spotted surface.

4. *Tin*.—It enters secondary metal through solder. The curve of Heycock and Neville⁶ and Arnemann,⁷ given in Fig. 9, shows an eutectic with 90 per cent Sn freezing at 198°C.; there is no solid solution at the zinc-end of the eutectic line. Tin makes spelter hard and brittle. According to Prost,⁸ the presence of tin to the extent of 0.01 per cent has little effect on the malleability; when the amount

¹ See also Mathewson-Trewin-Finkeldey, *Tr. A. I. M. E.*, 1920, LXIV, 305.

² *Metallurgie*, 1906, III, 477.

³ Prost, *loc. cit.*

⁴ *Zt. anorg. Chemie*, 1906, XLIX, 386.

⁵ Prost, *loc. cit.*

⁶ *J. Chem. Soc.*, 1897, LXXI, 383.

⁷ *Metallurgie*, 1910, VII, 201.

⁸ *Loc. cit.*

exceeds 0.01 per cent its effect is very decided, with 0.03 per cent rolling is impossible.

5. *Aluminum*.—The constitutional diagram of Rosenhain and Archbutt¹ and Bauer and Vogel,² Fig. 10, shows a hidden chemical compound C, Al_2Zn_3 , with approximately 85 per cent Zn at $443^\circ C.$, at the zinc-end of the curve an eutectic with 95 per cent Zn freezing at $380^\circ C.$, a solid solution of zinc with a maximum of 0.75 per cent Al at the eutectic line, and a transformation at $256^\circ C.$

An addition of a small quantity of Al up to 5 per cent to zinc³ has the effect of clearing the metal and thickening it instead of in-

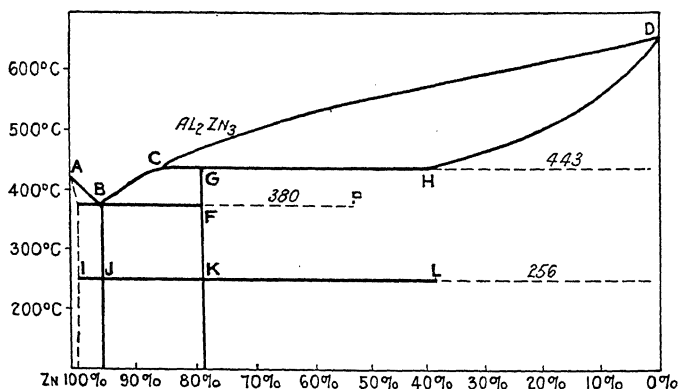


FIG. 10.—Alloy series Zn-Al.

creasing the fluidity, so that the temperature has to be raised; with 5.3 per cent Al and a temperature of $451^\circ C.$ perfect castings are obtained. The clearing of the metal bath⁴ by an addition of 0.01 per cent Al has been utilized in galvanizing iron; the coating is thinner, more uniform and brilliant, and holds its luster longer than in the absence of aluminum, also less dross is formed. The "aluminized zinc"⁵ is prepared by melting zinc in a graphite crucible and adding aluminum in small proportions with constant stirring until an alloy with 5 to 10 per cent Al has been formed which should

¹ *Philos. Trans. Roy. Soc.*, 1911, A, CCXI, 315; *J. Inst. Met.*, 1911, VI, 236.

² *Mitth. k. Materialprüfungsamt*, 1915, XXXIII, 146; *J. Soc. Chem. Ind.*, 1916, XXXV, 543.

³ Rigg-Morse, *Tr. Am. Inst. Met.*, 1915, IX, 26.

⁴ Richards, *Min. Ind.*, 1893, II, 11.

Turnbull, *J. Inst. Met.*, 1914, XII, 301.

⁵ *Aluminum World*, 1897, III, 81.

melt below $480^{\circ}\text{C}.$; this is then added in small lots of 2 lb. at a time to the zinc bath.

13. Corrosion.—Prost¹ who investigated the behavior of samples of commercial zinc (Pb 1.14 to 1.25, Cd 0.06 to 0.13, Fe 0.021 to 0.032 per cent) with sulphuric acid (0.5 per cent H_2SO_4), hydrochloric acid (0.372 per cent HCl), and brine (5 per cent NaCl) found with acids that if the amount of any impurity is increased beyond the normal, the corrosion is hastened; and that this is less accentuated by Pb than by Cd and by Fe. The presence of As, Sb or Sn even in small quantities greatly increases corrosion; this is especially the case with As and Sb. A salt solution does not appear to have a decided dissolving effect.

¹ *Rev. Un. Min.*, 1914, VI, 208.

CHAPTER IV

INDUSTRIAL USES AND ALLOYS

14. General.—The principal industrial uses of metallic zinc are: galvanizing, preparation of alloys, sheet metal, desilverization of lead bullion, and ornamental castings. In 1917 the domestic consumption of spelter was galvanizing 42.7, brass making 38.2, sheet rolling 12.8, lead desilverization 1.4, castings 0.5, other purposes 4.4 per cent. Blue powder and oxide serve as precipitating and reducing agents, as paint, and as raw materials for the preparation of salts: ZnSO_4 , ZnCl_2 , etc. There is a movement on foot in the United States¹ to increase the use of spelter for sheet metal and castings to bring the consumption to the one prevailing in Europe.

15. Galvanizing. General.²—Coating industrial iron with a thin layer of zinc belongs to a treatise on iron and steel; here only a brief outline of the leading features can be given.

16. Hot Galvanizing.³—This process consists in coating wrought-iron or soft-steel plate, wire, pipe,⁴ small articles, etc., by immersion with a thin coating of zinc to protect them from corrosion.

Galvanizing Sheets.—The leading operations are freeing the annealed iron from scale by immersing in acid (pickling), washing and drying; passing the cleaned sheet through a pot⁵ containing molten zinc, removing the excess zinc; washing, drying, and straightening the galvanized plate. The sheet is soft steel; the purer the steel, the better the coat and the smaller the consumption of zinc. Formerly the sheets were manipulated by hand, and hot hydrochloric acid (20 per cent HCl) served as pickle. In the United

¹ Editor, *Eng. Min. J.*, 1918, CVI, 705.

² Flanders, W. T., "Galvanizing and Tinning," David Williams Co., New York, 1916.

Sang, *Rev. Mét.*, 1912, IX, 1, 78, 161, 343.

Rawdon, *Tr. Am. Soc. Testing Materials*, 1918,¹ 217.

³ Galvano, *Metal Industry*, 1907, V, 75.

Cowper-Cowles, *Electrochem. Met. Ind.*, 1908, VI, 189.

Beckmann, *Rev. Mét. Extr.*, 1911, VIII, 429.

Poppleton, *Iron Age*, 1918, CI, 740; CII, 430, 502.

⁴ Buchert, *Stahl u. Eisen*, 1912, XXXII, 1487.

⁵ "Corrosion of Pot," *Eng. Min. J.*, 1915, C, 478.

States mechanical handling¹ has replaced manual labor; this has made possible the use of sulphuric acid (10 to 15 per cent H_2SO_4) heated with live steam to 70°C ., which acts more slowly than hydrochloric acid. The sheets are packed in acid-proof crates, which are provided with vertical pins to keep the sheets apart; a crate load weighs from 1 to 2 tons. The acid tanks are of pitch or yellow pine, and are hooded. They are about 5 ft. wide and 1 ft. longer and deeper than the largest sheet to be pickled. There are in use two types of machines for renewing the contact of sheet and acid, the oscillator and the Mesta plunger. The former resembles a jig with a wooden plunger (12 in. thick, 4 ft. deep, 26-in. stroke) placed either on the side or the end of the tank. The Mesta type, which is the more common apparatus, consists of a rotatable steam cylinder carrying four horizontal arms from which are suspended the crates. These are raised and lowered about 12 in. in succession in two tanks filled with acid, and one filled with water, placed in three quadrants of a circle; the fourth is reserved for loading and unloading the crates. Pickling and washing lasts about 40 min. The cleaned sheets are inspected and then stored in a tank filled with water for 72 hr. or longer, the water to be renewed frequently to prevent accumulation of acid. From the storage tank the sheets are removed 20 or 30 at a time into a solution tank, containing 0.5 to 1.0 per cent HCl , to be transferred as needed to the dipping apparatus.

There are two methods of dipping, flux- and dry-dipping. In the former the wet sheet is passed through a bath of flux ($\text{NH}_4\text{Cl} + \text{ZnCl}_2$) and then into the galvanizing machine. In dry-dipping the bath of flux is omitted; the wet plates are fed, as indicated in Fig. 11, by means of 6-in. rollers into a drying oven whence they are delivered by similar rolls to the galvanizing pot. The pot, riveted or welded steel or preferably cast steel, holds 25+ tons spelter; it is enclosed by brickwork and heated with coal from an external fireplace which is placed at one end and has a flue at the other; producer or oil gas allows a better control of temperature of bath, which lies between 400° and 480°C . The pot, provided with guides at in- and out-lets, has a frame with two or three pairs of 8-in. rolls. In the four-roll pot, shown in Fig. 11, one pair of rolls is entirely submerged, the other only partly so, the metal line being $\frac{1}{16}$ to $\frac{1}{4}$ in. below the surfaces of the rolls; in addition to drawing in the sheet, it wipes off the excess of zinc. On leaving the bath after an immer-

¹ Clement, *Stahl u. Eisen*, 1908, XXXV, 111, 937, "European Machines."

sion, the zinc on the surface of the plate crystallizes and gives it its characteristic *moiré* surface. The plate drops on to the conveyor which delivers it to the washing tank, a metal box with inclined bottom to allow sludge etc. to settle, and a pair of submerged rolls. From the wash-tank the sheet passes through guides into two pairs of 6-in. rolls, one rubber coated the other with ground finish, which deliver it to a cast-iron coke-fired box; at the exit are similar uncoated rolls which deliver the finished sheet on to a car where they are inspected.

Corrugated sheets are passed through suitable rolls after galvanizing.

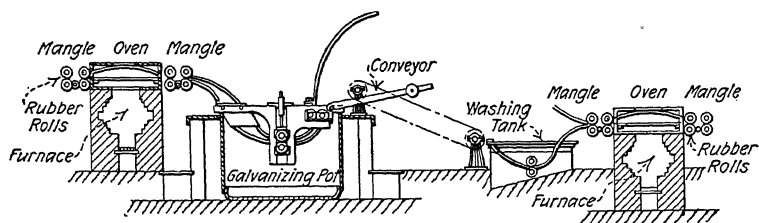


FIG. 11.—Sheet galvanizing plant.

The acid consumed is 6 to 7 per cent of weight of sheet, the loss of iron in pickling is about 1.5 per cent; there are formed 25 to 35 lb. hard zinc and 15 to 25 lb. oxide per ton of sheet, varying with the thickness. In galvanizing, it is essential that the spelter used be pure; aluminized zinc has been treated in §12.⁵ When zinc comes in contact with iron¹ it forms the compound FeZn_3 , Fig. 5, which connects the iron with the zinc coating; the FeZn_3 layers show some included crystals of FeZn_7 . The coating weighs from 0.75 to 2.00 oz. per square foot of iron.

In galvanizing *wire* the principles followed are the same as those with plate; the main difference is that the entire operation is continuous. From 12 to 30 coiled wires are drawn at a speed of 200 ft. per minute through an annealing furnace in which they are brought to redness, they pass at this temperature through the sulphuric acid pickle, then through sand that the surfaces may be brightened before they enter the zinc bath; the galvanized wires on leaving the pot are wound on drums. Galvanizing reduces the strength of the wire especially when subjected to torsion.²

¹ Guertler, *Internat. Zt. Metallographic*, 1911, 1, 353.

² Winter, *Internat. Congress Bergbau*, 1910, vol. Theoretisches Hüttenwesen, p. 195.

In galvanizing there are formed two by-products, iron-zinc alloy with 2 to 5 per cent Fe and skimmings, which have to be removed from the pot periodically. Their treatment is similar to that discussed in §§112 and 113. The pickling solution is neutralized with lime, the precipitate filtered, dried, calcined, and sold as paint.

17. Cold or Electrogalvanizing.¹—Electro deposition is taken up in §123. In electro galvanizing, the cathode is soft steel with a cleaned surface, the electrolyte a slightly acidified solution of zinc sulphate which may contain other salts, and the insoluble anode, lead or Acheson graphite.

The soft steel is cleaned in the same manner as is the case with hot galvanizing. The cleaned metal with its bright surface is transferred from the storage tank to the depositing vat. The electrolyte of Cowper-Coles is made up of 1 gal. water, 35 oz. pure crystalline zinc sulphate and 0.1 oz. sulphuric acid, which corresponds to 1,000 lb. water, 262.5 lb. pure crystalline sulphate, and 3.75 lb. of sulphuric acid; that of Sang of 1,000 lb. water, 900 lb. pure zinc sulphate, 300 lb. pure aluminum sulphate, made slightly acid with sulphuric acid, and grape sugar as an addition agent, as this gives brightness to the deposit. The temperature of the electrolyte is 25°C. A soluble anode of spelter, with or without 1 per cent Al, is used in many instances. It has the advantage of requiring only a low e.m.f., 0.6 volt, in the process; but two great drawbacks are, that when 50 per cent of the anode has been dissolved a large portion of the remainder crumbles away and drops, and that impurities are likely to get into the electrolyte which interfere with the character of deposit. Therefore an insoluble anode of lead or preferably Acheson graphite is more common in spite of the higher e.m.f. required, 3.2 volts with a current density of 15 amp. per square foot of cathode area. The depleted zinc content is restored by withdrawing electrolyte and passing it over a mixture of 2.5 lb. coke and 1.25 lb. cadmium-free blue powder (75 to 90 per cent metallic Zn) held in a filtering vat which has a filter of charcoal. The apparatus used varies with the form of the iron that is to be coated.

¹ Richter, C., "Die galvanische Verzinkung des Eisens," Leipsic, 1895.
Th. Cowper-Coles, "Electrolytische Verzinkung," Knapp, Halle, 1905.
Editor, *Electrochem. Met. Ind.*, 1907, v, 331.
Cowper-Coles, *op. cit.*, 1908, vi, 189.
Sang, *Rev. Mét.*, 1912, ix, 160.

18. Sherardizing or Dry Galvanizing.¹—This process, introduced by Sherard Cowper-Cowles in the United States in 1908, consists in charging cleaned iron into a drum with blue powder (35 to 45 per cent metallic Zn) dried at 250°C., and keeping the contents for from 30 min. to several hours at a temperature of 300° to 420°C., when the iron takes a dull light-gray coat of zinc which increases in thickness with temperature and time of treatment, and is capable of receiving a high polish. The articles most successfully treated are nuts, bolts, screws, nails, pipe fittings, small intricate castings which can not be perfectly coated by the older processes. The process taking place is one of cementation; microphotographs show above the iron an iron-zinc alloy followed by a zinc-iron alloy, and this by a layer of zinc. In one instance² the iron-zinc alloy was $\frac{1}{100}$ in. thick, the zinc-iron alloy $\frac{1}{100}$ in., and the zinc $\frac{1}{100}$ in.; the first is believed to resemble FeZn₃ (see Fig. 5) and the second FeZn₇ holding some Zn in solution. The higher the temperature, the more will FeZn₃ prevail over FeZn₇; the higher the iron-content, the lower is the resisting power to corrosion; the higher the zinc-content of the blue powder, the lower can be the temperature and the shorter the time of heating.

In practice small castings are freed from grease by treatment in lye (38 lb. caustic: 100 gal. water, 60° to 80°C., 10 min.), then washed with water (70° to 90°C.), pickled with hydrofluoric acid (5 per cent HF, 60° to 80°C.), washed, treated with milk of lime (20 lb. air-slaked lime to 100 gal. water) to neutralize the acid, washed, and air-dried. Small defects are removed by sand-tumbling for 5 to 10 min. Steel bolts, washers, nuts, etc. are cleaned as are castings, excepting that sulphuric acid is used for pickling. The heating

¹ Sang, *Electrochem. Ind.*, 1907, v, 187.

Cowper-Coles, *op. cit.*, 1908, vi, 191.

Burn-Murdoch, *Brass World*, 1909, v, 383.

General Electric Co., *Iron Age*, 1915, xcvi, 1108 (electric heating).

Burgess, *Sherardizing Magazine*, 1910, i, Nos. 10 and 11.

Sang, *Met. Chem. Ind.*, 1911, ix, 545.

Arthur-Walker, *J. Ind. Eng. Chem.*, 1912, iv, 397.

Johnson-Woolrick, *Tr. Am. Electrochem. Soc.*, 1912, xxi, 561.

Sang, *Rev. Mét.*, 1912, ix, 343.

Liggett, *Tr. Am. Foundrymen's Assoc.*, 1913, xxi, 187.

Trood, *Iron Age*, 1914, cxiv, 191, 245, 316, 378, 424; *Tr. Am. Inst. Met.*, 1915, ix, 101.

Storey, *Met. Chem. Eng.*, 1916, xiv, 683.

² *Brass World*, 1909, v, 384.

box is a boiler-iron cylinder, 18 in. in diameter and 60 in. long with side $\frac{3}{8}$ to $\frac{1}{8}$ in. thick, which holds a charge of about 1 ton. Several cylinders are rolled into a reverberatory furnace to be heated together. Single boxes, also of boiler iron, are 18 in. in diameter but not more than 36 in. long, they have 6 or 8 sides and cast-iron ends with trunnions, one of which is provided with a chain gear. A charge, made up of 3 to 5 lb. blue powder to 100 lb. iron, is held at 380° to 420°C. for 3 hr. or more; the treated box or boxes are removed from the furnace, allowed to cool in 10 to 20 hr. to 100°C.; the contents are discharged over a screen which removes the dust; the latter receives some fresh blue powder and is used for another charge.

19. Schoop Metallizing Process.¹—In galvanizing by this process a spray of atomized zinc is projected with force against iron which has been cleaned (sandblasted) and warmed, and forms an adhesive coat. The spraying apparatus (pistol) consists of a cubical box, $3\frac{1}{2}$ in., with handle and nozzle, weighing $3\frac{1}{2}$ lb., into which is fed in the form of wire the zinc to be atomized. Three pipes with oxygen, hydrogen, and air, under pressure, conduct the gases through the box into concentric tubes enclosed in the nozzle. The box contains an air-driven feeding- and wire-straightening device which leads the zinc at a speed of 12 ft. per minute through the nozzle core. The O-H blowpipe flame, containing an excess of H so as to be reducing, melts the zinc; the air in the central tube atomizes it and blows the atomized metal with a velocity of about 3,000 ft. per second onto the object to be galvanized which is held at 5 to 6 in. from the nozzle. The zinc wire remains cold and unaltered until within $\frac{1}{32}$ in. from the nozzle tip. The sprayed metal is cooled sufficiently by the expansion of the atomizing air that it may be directed for a moment upon the hand without injury, and continuously upon inflammable materials, such as paper, cloth, and wood. It is supposed that the heat set free by the impact of the metal upon the hard surface, momentarily

¹ Gradenwitz, *Eng. Min. J.*, 1911, XCI, 532.

Editor, *Iron Age*, 1914, XCIV, 426.

Morcom, *Eng. Min. J.*, 1915, C, 192.

Editor, *op. cit.*, 1916, CII, 111.

Guenther, H—Schoop, M. U., "Das Schoopsche Metallspritzverfahren, etc.," Frank, Stuttgart, 1917.

Arnold, *Met. Ind.*, 1918, XII, 121.

Matzinger, *Electrotechnik u. Maschinenbau*, 1818, p. 69; *Chem. Abstr.*, 1918, XII, 2305.

Arnold, *Zt. angew. Chem.*, 1918, XXI¹, 15; *Chem. Abstr.*, 1918, XII, 2305.

vaporizes the metal which then condenses and solidifies and penetrates the surface to some extent. The specific gravity of the coating falls as the distance of the object to be coated increases from the pistol;¹ thus, with specific gravity of molten zinc 6.922, that of the metal sprayed at a distance of 3.15 in. is 6.325, of 16.54 in. is 5.903. Spraying with lead is said to cost from 1 to 2 cts. per square foot.

20. Properties of Zinc Coatings.²—In hot galvanizing, the coat of zinc is usually 28 gr. per square foot, but is not uniform, the surface is spangled; the process, however, is cheap, and is used mainly with sheet and wire. In cold galvanizing, the coat of zinc is usually 14 gr. per square foot and uniform, but has a matted frosty appearance; it adheres better to the iron than is the case with the hot process and is less readily corroded, provided the work has been well done; the process is expensive, is used with wire and small articles. In sherardizing, the coat is of uniform thickness and of similar appearance to that of the cold process; its adherence is better than that of either hot or cold galvanizing; the process is suited mainly for small articles.

21. Sheet Zinc.—It has been shown in §4 that zinc can be rolled and drawn at 100° to 150°C., and that according to the research of Prost and Van de Castele,³ Cd in excess of 0.25 per cent, As 0.02 per cent, Sb 0.07 per cent, Sn 0.01 per cent, Cu 0.08 per cent, Fe 0.12 per cent are harmful, while Pb up to 1.25 per cent facilitates the operation, and that the presence of two or more impurities accentuates the injurious effect of each. The mechanical properties of sheet zinc of different degrees of purity have been studied by Meyer.⁴ Sheet zinc, which is used very extensively in Europe as roofing material,⁵ has not as yet found such general employment in the United States. It serves for gutters, spouts, piping, bath tubs, wash-boards, etc. Thin sheets are serviceable in the form of stamped ornaments, in zincography and plate etching; zinc shavings serve as a precipitant of precious metal from cyanide solution, for this purpose the sheets are mounted on a mandrel and the shavings

¹ Arnold, *loc. cit.*

² Burgess, *Electrochem. Ind.*, 1905, III, 17.

Cowper-Coles, *op. cit.*, 1908, VI, 189.

Burgess, *Sherardizing Magazine*, 1910, I, Nos. 10 and 11.

³ *Rev. Un. Min.*, 1913, II, 31; *Eng. Min. J.*, 1913, xcvi, 818.

⁴ *Oest. Zt. Berg. Hüttenw.*, 1905, LIII, 522, 538.

⁵ Seamon, *Eng. Min. J.*, 1918, CVI, 620.

spirals with a side-cutting tool, they are $\frac{1}{8}$ to $\frac{1}{4}$ in. wide and $\frac{1}{16}$ to $\frac{1}{8}$ in. thick. Many other uses have been proposed.¹ In the rolling establishments there are distinguished sheet and plate mills; the former furnish large sheets, the latter small plates which are cut into sizes demanded by the various trades. The material for the former is spelter in standard-size cakes, that for the latter special-size castings or cut-up sheets from the sheet

The Belgian method of rolling sheets² is as follows: The metal is taken from the refining furnace into a plate of definite size; this is allowed to cool until it attains a temperature ranging from 120° C., is then seized with tongs, placed on the table of a two-stand-reversing rough-rolling plate mill, and rolled in several passes down to a sheet 0.2 in. in thickness. The rolls are 19.6 in. in diameter and 55.12 in. long. The bottom roll is fixed, has a flywheel 3 ft. in diameter, weighs 40 to 50 tons, and is connected with the top roll which is balanced, and adjusted by top-screws rotated by hand-wheel through bevel gears. The lower roll makes 40 to 60 r.p.m. and requires at least 100 hp. The sheets from the roughing mill are trimmed and heated in a furnace. A number of sheets, 7 or more in a pack, are then passed through the finishing rolls which have the same construction as the roughing rolls; they make, however, 32 to 38 r.p.m. The finished sheets are trimmed, weighed, numbered, and marked with a number corresponding to their thickness. Table 9 gives the numbers, thicknesses and average weights of the sheet-zinc gages.

American practice is similar to the Belgian. The first industrial zinc was rolled in the United States in 1866 by Matthiessen and F. W. Taylor. The rolling industry is concentrated in a few firms. In 1912 there were in operation nine sheet mills; for a great many years the Matthiessen & Hegeler Co., La Salle, Ill., and the Illinois Zinc Co., Peru, Ill., were the only plants producing sheet zinc. Crude spelter is melted in a reverberatory, built into a boiler and lined with brickwork, and fired from both ends. Furnaces

¹For, *Eng. Min. J.*, 1918, CVI, 705.

²Chewson-Trewin-Finkeldey, *Tr. A. I. M. E.*, 1920, LXIV, 305.

³Sart, *Rev. Un. Min.*, 1871, XXX, 201; *Berg. Hüttenm. Z.*, 1872, XXXI, 197, 3, 271.

⁴St. E., "Cours de Métallurgie des Métaux autres que le fer," Béranger, 1912, p. 148.

⁵Enthal, *Metal Industry*, 1918, XVI, 556.

TABLE 9.—SHEET-ZINC GAGES

Gage number	American		Belgian		Vielle Montagne	
	Thick-ness, deci-mals of an inch	Weight per square foot, pounds	Thick-ness, deci-mals of an inch	Weight per square foot, pounds	Thick-ness deci-mals of an inch	Weight per square foot, pounds
1	0.002	0.075	0.0018	0.068	0.004	0.150
2	0.004	0.150	0.0036	0.135	0.006	0.225
3	0.006	0.225	0.0055	0.206	0.007	0.263
4	0.008	0.300	0.0073	0.274	0.008	0.300
5	0.010	0.375	0.0091	0.341	0.010	0.375
6	0.012	0.450	0.0110	0.413	0.011	0.413
7	0.014	0.525	0.0128	0.480	0.013	0.488
8	0.016	0.600	0.0146	0.548	0.015	0.563
9	0.018	0.675	0.0165	0.619	0.018	0.675
10	0.020	0.750	0.0180	0.675	0.020	0.750
11	0.024	0.900	0.0217	0.814	0.023	0.863
12	0.028	1.050	0.0254	0.953	0.026	0.975
13	0.032	1.200	0.0290	1.088	0.029	1.088
14	0.036	1.350	0.0326	1.223	0.032	1.200
15	0.040	1.500	0.0364	1.365	0.038	1.425
16	0.045	1.688	0.0400	1.500	0.043	1.613
17	0.050	1.875	0.0437	1.639	0.048	1.800
18	0.055	2.063	0.0478	1.793	0.053	1.988
19	0.060	2.250	0.0509	1.909	0.058	2.175
20	0.070	2.625	0.0581	2.179	0.063	2.363
21	0.080	3.000	0.0728	2.730	0.070	2.625
22	0.090	3.375	0.0764	2.865	0.077	2.888
23	0.100	3.750	0.0800	3.000	0.084	3.150
24	0.125	4.688	0.0896	3.360	0.091	3.413
25	0.250	9.375	0.0992	3.720	0.098	3.675
26	0.375	14.063	0.1088	4.080	0.105	3.938
27	0.500	17.750				
28	1.000	37.500				

hold from 30 to 200 tons metal. This is dipped from the furnace, or from a kettle connected with the furnace, by means of a suspended ladle and cast into molds on a horizontal turntable or a car. The solidified slabs, e.g., 13.5 by 40 by 1.5 in. weighing 208 lb., are

transferred to an annealing furnace. From this they pass through two-high roughing rolls, *e.g.*, 22 by 49½ in. with 30-ton flywheel and 350-hp. engine. The resulting sheet is trimmed and goes in suitable size to the finishing rolls, also two-high, where it is rolled to the desired thickness. During the stages in rolling, the plates leaving the rolls are wound up in coils to facilitate handling and permit slow cooling.

The American Zinc Products Co., Greencastle, Ind.,¹ rolls daily 1,000 to 1,500 tons of zinc plate. A refining furnace holds 100 tons spelter; the metal is drossed and cast into 1-in. plates; at intervals accumulated lead is tapped. The cast plates are annealed and passed through 24-in. roughing rolls; the resulting sheets are sheared, stacked in packs on steel cars, and go to pack annealing furnaces in which the temperature is regulated by recording pyrometers. Thence, the packs go to finishing rolls, 24 by 72 in., provided with automatic motor-operated lifting tables. The finished sheets are trimmed by rotary slitting shears.

22. Zinc Castings.—The use of cast zinc is somewhat limited in this country (ornaments, statues, blocks for hats); however, there are many ways in which it could and probably will be used² more extensively than at present, *e.g.*, as hardware and electric fuses. Zinc contracts slightly upon solidification; the shrinkage is 0.3125 in. per foot. When cast at a high temperature, it is brittle; when cast near the freezing point, it is slightly malleable. An addition of 0.001 per cent aluminum in the form of thin sheet clippings³ increases the fluidity; ammonium chloride is frequently used as flux, it is sprinkled sparingly over the molten metal and stirred into the dross. Thin ornamental castings are made by the slush process⁴ in which the liquid metal is poured back into the ladle as soon as the metal in contact with the mold has set. The castings are polished, plated, or finished in other suitable ways. The molds are usually made of bronze, the insides are covered with soot from turpentine smoke, the pouring temperature lies between 440° and 450°C. It is essential that the spelter be pure; Cd in excess of 0.05 per cent makes the casting hot short and causes cracking; Pb in excess of 0.20 per cent causes weakening and thickening of the casting;

¹ Dietz, *Eng. Min. J.*, 1918, CVI, 778.

² Editor, *Eng. Min. J.*, 1918, CVI, 705.

³ Anon., *Foundry*, 1915, XLIII, 232.

⁴ Stone, *Tr. Am. Inst. Met.*, 1914, VIII, 186.

Rigg-Morse, *op. cit.*, 1915, ix, 26.

Fe makes the metal viscous; As acts similarly, the limit of each is 0.1 per cent; the effect of these metals is cumulative. The harmful influence of Cd is so characteristic that slush castings are made to test for the purity of the spelter. Zinc rods which are used in galvanic cells, are made by casting or by extruding. Die-castings are taken up below.

23. Zinc Alloys.—Zinc is present in a large number of alloys, e.g., brass, german or nickel silver, etc.; alloys in which zinc is the preponderating metal are few in number, some of these alloys with zinc base¹ are antifriction or white metal, bearing metal, die castings, babbit. Table 10 gives compositions.

TABLE 10.—ZINC ALLOYS

Name	Zn	Cu	Pb	Sb	Sn	Al	Reference
Antifriction metal.....	85.0	5.0		10			1
Antifriction metal.....	80.0	5.5			14.5		1
Antifriction metal.....	76.0	5.5			18.5		1
Lumen bearing metal....	86.0	10.0				4	2
Lumen bearing metal....	82.0	12.0				6	3
English bearing metal....	67.7	7.4			14.9		4
Die-casting.....	84.5	4.5			9.0	2	5
Die-casting.....	70 to 90	2 to 5	0 to 2	0 to 2	0 to 20	0 to 5	5
Babbit.....	60.0		5	3	19.0		6

1. Ledebur-Bauer, "Die Legierungen," Krayn, Berlin, 1920.

2. Lake, *Iron Age*, 1911, LXXXVIII, 532.

3. Law, "Alloys," Lippincott, Philadelphia, 1919.

4. Campbell, *Tr. A. I. M. E.*, 1912, XLIV, 845.

5. Cowan, *Tr. Am. Inst. Met.*, 1914, VIII, 202.

6. Charpy, "Contributions à l'étude des alliages," Chamerot-Renouard, Paris, 1901, 208.

24. Blue Powder and Zinc Oxide.—Blue powder produced incidentally (§§72, 115) in the condensation of zinc vapor, is often prepared especially for use as a precipitating agent of gold and silver from cyanide solution, in sherardizing, and chemical industries, such as the manufacture of aniline dyes, the preparation of indigo and of hydrogen for military balloons (heating with lime), the purification of sugar, distillation industries. The standard

¹ Guillet-Bernard, *Rev. Mét.*, 1918, XV, 407; *Iron Age*, 1919, CIII, 175; *Chem. Met. Eng.*, 1919, XX, 645.

Jarés, *Zt. Metallkunde*, 1919, X, 1.

product contains 90 per cent Zn as an impalpable powder and 10 per cent ZnO; the commercial article is frequently richer in ZnO. Care has to be taken in packing and storing blue powder, as there is danger of its taking fire when exposed to moist air. Zinc oxide is used largely as paint, it is mixed with white lead to give it better wearing properties; it is used in the manufacture of automobile and truck tires, of oil cloth and linoleum, in glass and clay works, for the preparation of salts, with zinc chloride as cement, etc. The production of pure and leady zinc oxide is taken up in §137.

CHAPTER V

ZINC COMPOUNDS

25. Zinc Oxide, ZnO . (80.26 per cent Zn; $65.37\text{Zn} + 16\text{O} = 81.37\text{ZnO} + 84,800 \text{ cal.}$).—It occurs as zincite, a deep-red to orange-yellow lustrous hexagonal mineral containing some Fe and Mn; is formed by the burning of Zn, the calcination of ZnCO_3 and of ZnSO_4 , the roasting of ZnS , and the treatment of oxide ores (Wetherill process, §141). The oxide prepared by these

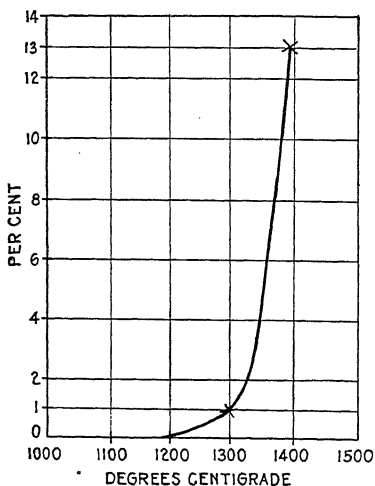


FIG. 12.—Volatilization of zinc oxide.

methods is an amorphous white powder; the crystalline (hexagonal) oxide, also white, is found in furnace accretions¹ and is formed by calcining $\text{Zn}(\text{NO}_3)_2$; amorphous ZnO becomes crystalline when heated, it changes its color to yellow and pales largely upon cooling. Heating amorphous ZnO in a muffle or reverberatory furnace to $1,000^\circ\text{C}$. for 2 or 3 hr., renders it crystalline and compacts it so that it can be readily charged into retorts.² Zinc oxide prepared by calcining ZnCO_3 has a specific gravity of 5.42;³ the figures given for

¹ *Oest. Zt. Berg. Hüttenw.*, 1899, XLVII, 443.

² Pape, *Eng. Min. J.*, 1910, LXXXIX, 874; U. S. patent No. 947,399, January 25, 1910.

³ Brügelmann, *Wiedemann Annal*, 1878, IV, 283.

⁴ Kopp, *Liebig Ann. Suppl.*, 1864-65, III, 289.

⁵ *Berg. Hüttenm. Z.*, 1875, XXIX, 70.

⁶ *Metallurgie*, 1916, III, 212, 233.

shows that ZnO is volatile above, $1,000^{\circ}\text{C.}$ and rapidly at $1,300^{\circ}$. Data by Kowalke¹ show that volatilization begins at $1,300^{\circ}\text{C.}$ and is complete between $1,370^{\circ}$ and $1,400^{\circ}\text{C.}$ The dissociation temperature into Zn and O has been calculated by Stahl² as $3,817^{\circ}\text{C.}$

ZnO is reduced to Zn by C, CO, and H at elevated temperatures.³ The reduction of ZnO by C is said by Hempel⁴ to begin below the boiling point of Zn (920°C.) and to be completed only at about

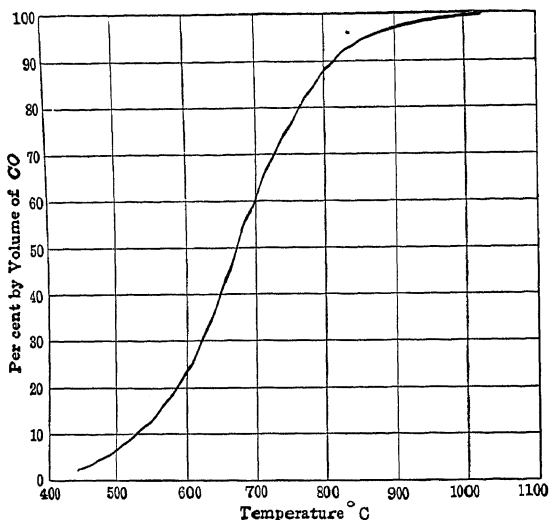


FIG. 13.—Equilibrium curve for CO and CO_2 with C at different temperatures.

$1,300^{\circ}\text{C.}$; Prost⁵ gives $1,075^{\circ}\text{C.}$ as the temperature of pure ZnO; Boudouard⁶ found steady reduction to take place between $1,125^{\circ}$ and $1,150^{\circ}\text{C.}$, the issuing gas to contain CO 99, CO_2 1 per cent vol.; Doeltz-Graumann,⁷ by heating ZnO and cane sugar in a tube closed at one end between 950° and $1,000^{\circ}\text{C.}$, obtained a loss in

¹ *Tr. Am. Electrochem. Soc.*, 1912, XXI, 557; *Met. Chem. Eng.*, 1912, X, 300.

² *Metallurgie*, 1907, IV, 690.

³ Lemarchands, *Rev. Mét.*, 1920, XVII, 803.

Jaenecke, "Physical Chemical Considerations," *Metall u. Erz*, 1919, XVI, 247.

Ravner, *Chem. Met. Eng.*, 1921, XXIV, 885.

⁴ *Berg. Hüttenm. Z.*, 1893, LII, 358.

⁵ *Bull. Assoc. Belg. Chim.*, 1896, X, 246-263; *Min. Ind.*, 1896, V, 596.

⁶ *Am. Chim. Phys.*, 1901, XXIV, 74; *Bull. Soc. Chim.*, 1901, XXV, 282; *Berg. Hüttenm. Z.*, 1902, LVI, 267.

⁷ *Metallurgie*, 1907, IV, 290.

weight ranging from 0.1 to 3.1 per cent, in a tube open at both ends with a current of N passing, a loss in weight reaching about 16 per cent. According to Johnson¹ the reduction temperature varies with the character of the oxide and the reducing carbon, and ranges from 1,007° to 1,108°C. Calcined oxide is easier of reduction than roasted blende; the temperature in furnace work is usually 1,100°C. The reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ is non-reversible; the reaction $2 \text{ZnO} + \text{C} \rightleftharpoons \text{Zn}_2 + \text{CO}_2$ is reversible.² The experiments of Ernst³ have shown that C above 995°C. burns exclusively to CO, if therefore the reduction temperature is held at 1,100°C. no CO₂ ought to form. In order to correct the accidental presence of some CO₂, there must be used an excess of C over that expressed by the first equation, which will readily reduce CO₂ to CO. Figure 13, representing the equilibrium curve of Boudouard⁴ for CO₂ and CO with C at different temperatures, shows that at 1,100°C.

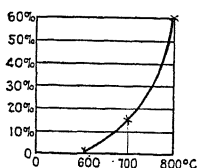


FIG. 14.—Reduction of ZnO by C.

the reduction of CO₂ by C to CO is practically complete. The reduction of ZnO by CO takes place according to $\text{ZnO} + \text{CO} \rightleftharpoons \text{Zn} + \text{CO}_2$. The curve of Doeltz-Graumann,⁵ Fig. 14, shows that the reduction of pure ZnO begins at 600°C. and reaches 60 per cent at 800°C., the figures representing losses in weight. Unless the resulting CO₂ is removed about as quickly as formed, the reaction will go from right to left; if this is done, the zinc vapor will be collected as powder. As a reducing agent, CO acts only as intermediary between C and ZnO, and the CO₂ is reduced to CO about as quickly as it is formed. The research of Lencauchez⁶ shows that a gas with 99.5 per cent vol. CO and 0.5 CO₂ exerts an oxidizing effect on zinc vapor at the temperature of its condensation, i.e., 500° to 700°C., also that an iron blast-furnace gas with 24 per cent vol. CO and 12CO₂ readily reduced ZnO at a white heat (1,150°C.), but reoxidized it at a cherry-red (700°C.). The equilibrium curve of Fulton,⁷ Fig. 15, for temperatures ranging from 500° to 740°C., indicates that much larger percentages of

¹ *Tr. A. I. M. E.*, 1913, XLVII, 219.

² Bodenstein, *Chem. Z.*, 1917, XLI, 9; *Chem. Abstr.*, 1917, XI, 2656.

³ Hofman, "General Metallurgy," 1918, 295, curve.

⁴ *Ann. chim. et phys.*, 1901, XXIV, 28.

⁵ *Metallurgie*, 1907, IV, 293.

⁶ *Mem. Soc. Ingén. civ.*, 1877, p. 575.

⁷ *Tr. A. I. M. E.*, 1919, LX, 293.

CO₂ are permissible than indicated by Lencauchez; in fact gases issuing from the mouths of condensers¹ contain often over 1 per cent CO₂ without exerting any oxidizing effect. The reduction of ZnO by C or CO is endothermic,

1. $\text{ZnO} + \text{C} = \text{Zn} + \text{CO} - 55,240 \text{ cal.}$
2. $2\text{ZnO} + \text{C} = 2\text{Zn} + \text{CO}_2 - 71,600 \text{ cal.}$
3. $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2 - 16,360 \text{ cal.}$
4. $\text{CO}_2 + \text{C} = 2\text{CO} - 36,880 \text{ cal.}$

hence, extraneous heat has to be supplied for the reducing agent to act. Reaction (3) consumes the smallest amount of heat, $-16,360$

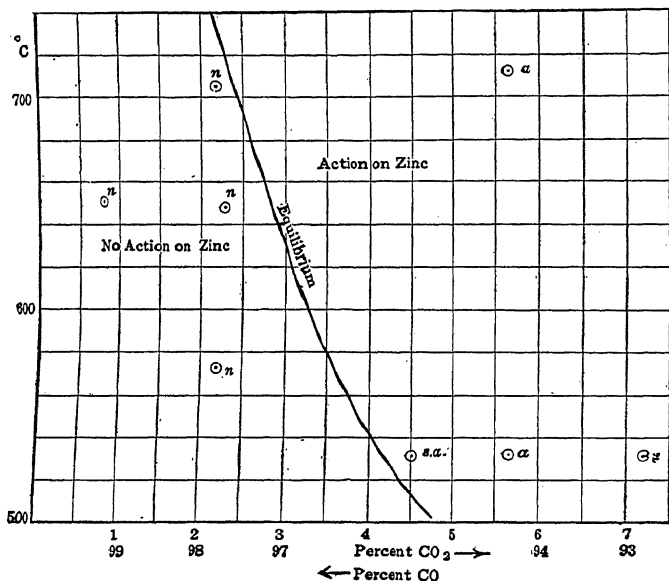


FIG. 15.—Equilibrium curve of the reaction $\text{Zn} + \text{CO}_2 \rightleftharpoons \text{ZnO} + \text{CO}$.

cal.; as, however, the CO₂ produced has to be reduced to CO by C which consumes $-36,880$ cal., there is no advantage; the sum of calories of Equations (3) and (4) is equal to that of Equation (1).

Zinc oxide is reduced by H according to $\text{ZnO} + \text{H}_2 \rightleftharpoons \text{Zn} + \text{H}_2\text{O} - 26,340 \text{ cal.}$ Reduction begins at $454^\circ\text{C}.$ ² but the water formed has

¹ Fischer, *Dingler Polytechn. J.*, 1880, CCXXXVII, 387; *Berg. Hüttenm. Z.*, 1880, XXXIX, 371.

² Firket, *Ann. Min. Belg.*, 1901, VI, 49.

to be removed as quickly as formed¹ as it reacts with the zinc vapor. The reaction has no practical value.

ZnO is reduced by Fe at the boiling point of Zn (920°C.). The reaction is reversible, $x\text{ZnO} + y\text{Fe} = x\text{Zn} + \text{Fe}_y\text{O}_x$, but the details are not known. In a retort containing roasted blende rich in Fe_2O_3 , the Fe_2O_3 has an oxidizing effect upon Zn-vapor; it has to be reduced to Fe before the temperature of the charge reaches 1,100°C. if a satisfactory yield of zinc is to be obtained. Sulphur has reducing effect upon ZnO, *viz.* $2\text{ZnO} + \text{S} = \text{ZnO}_2 + \text{SO}_2$.² The reaction, however, is imperfect.³ ZnO is soluble in acids and caustic alkali, less readily in caustic ammonia than in the sesquicarbonate;⁴ it is insoluble in water.

It forms with some metallic oxides fusible compounds or mixtures.⁵

Zinc hydroxide, $\text{Zn}(\text{OH})_2$ is a whitish powder only slightly soluble in water. It is precipitated from acid solution by caustic alkali and is soluble in the excess of the precipitant; it is also precipitated by milk of lime or magnesia. It has the property of acting as an acid with alkali and alkali earths forming zincates: K_2ZnO_2 , Na_2ZnO_2 , $\text{Sr}(\text{HZnO}_2)_2 + 7\text{H}_2\text{O}$, $\text{Ba}(\text{HZnO}_2)_2 + 7\text{H}_2\text{O}$, $\text{Ca}(\text{HZnO}_2)_2 + 4\text{H}_2\text{O}$.⁶

26. Zinc Carbonate, ZnCO_3 (52.02 per cent Zn; $81.37\text{ Zn} + 44.05\text{ CO}_2 = 125.42\text{ ZnCO}_3 + 15,500\text{ cal.}$).—The neutral carbonate occurs as smithsonite. The white precipitates formed by treating zinc solutions with alkali carbonates are basic carbonates, the proportions of ZnCO_3 and $\text{Zn}(\text{OH})_2$ varying with the concentrations of the solutions, the temperature, and the amount of precipitant used. Carbonates are readily soluble in acids. ZnCO_3 is decomposed into ZnO and CO_2 at 395°C. when heated in a closed tube.⁷

27. Zinc Sulphate, ZnSO_4 (40.49 per cent Zn; $81.37\text{ Zn} + 80.06\text{ SO}_3 = 162.43\text{ ZnSO}_4 + 52,900\text{ cal.}$).—Occurs as zinkosite, but the mineral is rare. Is formed with ZnO in roasting ZnS, by dehydrating zinc vitriol (see below), by slowly evaporating zinc vitriol in concentrated sulphuric acid. The pure salt is white, has a specific

¹ Deville, *Ann. phys. chim.*, 1855, XLIII, 7.

Dick, Percy, "Metallurgy," 1861, p. 535.

Rivot-Deville, *Ann. phys. chim.*, 1855, XLIII, 477.

² Newton, *Chem. News*, 1897, LXXV, 133.

³ Senderens, *Compt. rend.*, 1887, CIV, 58.

⁴ Hofman, *Tr. A. I. M. E.*, 1913, XLVII, 88.

⁵ Percy, "Metallurgy," 1861, p. 539.

⁶ Bertrand, *Compt. rend.*, 1892, CXV, 939, 1,028.

⁷ Friedrich-Smith, *Stahl u. Eisen*, 1911, XXXI, 1909; *Metallurgie*, 1912, IX, 409.

gravity 3.40, and an acid taste ZnSO_4 heated¹ in a current of air gives off some SO_3 at 702°C ., and does it readily at 720°C . being converted into $3\text{ZnO} \cdot 2\text{SO}_3$, which is white, hot and cold. Upon raising the temperature decomposition of this basic salt begins at 755°C ., and proceeds rapidly at 767°C . the remaining ZnO is yellow while hot, and white when cold. Other data are given in the reference. Heating ZnSO_4 with C to 528°C .² causes a partial decomposition according to $2\text{ZnSO}_4 + \text{C} = 2\text{ZnO} + 2\text{SO}_2 + \text{CO}_2$. Under the most favorable conditions, the 19.86 per cent in the ZnSO_4 are reduced to 3.47 per cent; of this total, 1.41 per cent are sulphide—and 2.06 sulphate—S. At a higher temperature ZnSO_4 is completely reduced to ZnS . The presence of SiO_2 has no effect upon dissociation, Fe_2O_3 lowers it, CaO has a decomposing effect.³ Heating ZnSO_4 in a current of steam⁴ to a temperature 100°C . lower than that of dissociation causes the reaction $\text{ZnSO}_4 + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2\text{SO}_4$ to take place.

28. **Zinc Vitriol**, $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ (22.65 per cent Zn; $81\text{ZnO} + 80\text{SO}_3 + 7 \times 18\text{H}_2\text{O} = 281\text{ZnSO}_4 + 7\text{H}_2\text{O} + 74,240 \text{ cal.}$).—Occurs as goslarite, is formed by the action of H_2SO_4 upon Zn or ZnO . It forms orthorhombic crystals which are white, transparent to translucent, brittle, and have an astringent metallic taste.⁵ The solubility as determined by Poggiale⁶ is given in Table 11.

TABLE 11.—SOLUBILITY OF ZINC SULPHATE IN WATER

Degrees Centigrade	ZnSO_4	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	Degrees Centigrade	ZnSO_4	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$
0	43.02	115.22	60	74.20	313.48
10	48.36	138.21	70	79.25	369.36
20	53.13	161.49	80	84.60	442.62
30	58.40	190.90	90	89.78	533.02
40	63.52	224.05	100	95.03	653.59
50	68.75	263.84			

¹ Hofman-Wanjudow, *Tr. A. I. M. E.*, 1912, XLIII, 551.

² Hofman, *Tr. A. I. M. E.*, 1905, XXXV, 830.

³ Mostowitsch, *Metallurgie*, 1911, VIII, 763.

⁴ Thomas, *Metallurgie*, 1910, VII, 610.

⁵ "Evaporation Solutions," Hampe, *Berg. Hüttenm. Z.*, 1891, I, 184.

"Production in Harz Mountains," Kerl, *Min. Ind.*, 1895, V, 83.

⁶ *Ann. chim. phys.*, 1845, VIII, 467.

42 METALLURGY OF ZINC AND CADMIUM

The specific gravities of solutions with increasing percentages of $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ are given in Table 12.

TABLE 12.—SPECIFIC GRAVITIES OF SOLUTIONS OF ZINC SULPHATE

$\text{ZnSO}_4 + 7\text{H}_2\text{O}$, per cent	Specific gravity	
	at 15°C. ¹	at 20.5°C. ²
5	1.0288	1.0289
10	1.0593	1.0588
15	1.0905	1.0899
20	1.1236	1.1222
25	1.1574	1.1560
30	1.1933	1.1914
35	1.2315	1.2285
40	1.2709	1.2674
45	1.3100	1.3083
50	1.3532	1.3511
55	1.3986	1.3964
60	1.4451	1.4439

The electric conductivity, as determined by Kohlrausch, is given in Table 13.

TABLE 13.—ELECTRIC CONDUCTIVITY OF ZINC SULPHATE SOLUTIONS³

ZnSO_4 , per cent	Per cubic centimeter in reciprocal ohms at 18°C.
5	191
10	321
15	415
20	468
25	480
30	444

An e.m.f. of 2.35 volts is required to decompose ZnSO_4 into Zn and SO_4 . Heated in a current of air, $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ is changed at 25°C. into $\text{ZnSO}_4 + 6\text{H}_2\text{O}$, at 28° into $\text{ZnSO}_4 + 2\text{H}_2\text{O}$, at 115° into $\text{ZnSO}_4 + \text{H}_2\text{O}$, and 225° into ZnO .⁴

¹ Gerlach, *Fresenius, Zt. analyt. Chemie*, 1860, VIII, 260.

² Schiff, *Ann. Chem. Pharm.*, 1859, CX, 72.

³ Landolt-Börnstein-Roth, "Physikalische Tabellen," Springer, Berlin, 1912.

⁴ Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 551.

29. Zinc Sulphite, ZnSO_3 (44.88 per cent Zn; $81\text{ZnO} + 64\text{SO}_2 = 145\text{ZnSO}_3 + 20,540 \text{ cal.}$, in dilute solution, $30,540 \text{ cal.}$).—The salt is formed by the action of H_2SO_3 upon Zn or ZnO; it crystallizes as $2\text{ZnSO}_3 + 5\text{H}_2\text{O}$, is soluble with difficulty in H_2O , readily so in H_2O containing H_2SO_3 , insoluble in alcohol. Heated in a closed vessel to 200°C. , there are given off H_2O and SO_2 , the residue consisting of ZnSO_4 , ZnO and ZnS; exposed to air it readily oxidizes to ZnSO_4 . The use of ZnO has been suggested by Schnabel¹ for absorption of dilute SO_2 from roaster gases, the SO_2 to be driven off as concentrated gas by heating the ZnSO_3 . Electrolysis of ZnSO_3 requiring a lower e.m.f. than ZnSO_4 , its formation followed by electrolysis has been suggested by Kosmann² for the treatment of mixed sulphide zinc ores; also by Rees and Sulman.³

30. Zinc Silicates.—The singulosilicate, Zn_2SiO_4 , occurs as willemite (56.61 per cent Zn; $162.74\text{ZnO} + 60.3\text{SiO}_2 = 223.04\text{Zn}_2\text{SiO}_4 - 23,760 \text{ cal.}$); the bisilicate, ZnSiO_3 , is not found as mineral (40.84 per cent Zn; $81.37\text{ZnO} + 60.3\text{SiO}_2 = 141.67\text{ZnSiO}_3 + 8,800 \text{ cal.}$); the hydrosingulosilicate, $\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$, occurs as calamine. The singulosilicate melts at $1,500^\circ\text{C.}$, the bisilicate at $1,437^\circ\text{C.}$ ⁴ Earlier determinations by Stein⁵ gave $1,488^\circ\text{C.}$ for Zn_2SiO_4 and $1,479^\circ$ for ZnSiO_3 . In heating ZnO with SiO_2 , Percy⁶ obtained fused masses only at the melting point of platinum ($1,755^\circ\text{C.}$); Prost⁷ fused ZnSiO_3 at $1,500^\circ\text{C.}$ Reduction by means of C requires a high temperature; Prost⁸ obtained a partial reduction at $1,250^\circ\text{C.}$, and reduced all the zinc at $1,500^\circ$. Ores containing zinc silicates therefore require a higher temperature than those which contain oxide.

31. Zinc Aluminate, $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ (35.61 per cent Zn).—Occurs as gahnite (zinc spinel), part of the ZnO being replaced by FeO, MnO or MgO, and part of the Al_2O_3 by Fe_2O_3 . Zinc aluminate prepared by Ebelmen⁹ by fusing Al_2O_3 , ZnO, and B_2O_3 , had the form of octahedral crystals which were transparent, colorless, and

¹ *Zt. B. H. S. W. i. P.*, 1881, XXIX, 395; *Berg. Hüttenm. Z.*, 1882, XLI, 156, 449.

² *Berg. Hüttenm. Z.*, 1892, LI, 439.

³ *Eng. Min. J.*, 1913, XCVI, 1017.

⁴ Jaeger-Van Klooster, *Proc. akad. Wetenschappen*, 1916, XVIII, 896, through *Chem. Abstr.*, 1916, X, 1476.

⁵ *Zt. anorg. Chemie*, 1907, LV, 159.

⁶ "Metallurgy," 1861, p. 536.

⁷ "Métallurgie des Métaux, etc.," 1912, p. 14.

⁸ *Loc. cit.*

⁹ *Ann. chim. phys.*, 1851, XXXIII, 34.

scratched glass; it was obtained by Smith¹ by heating ZnO and Al₂O₃ in a Deville furnace, the product was a compact, gray, stony substance which scratched flint glass. Stelzner-Schulze² found in the altered part of an old retort bluish zinc spinel of the composition Zn 42.60, FeO 0.12, Al₂O₃ 55.61 per cent. They discovered it also in basic slags of Freiberg lead blast furnaces which ran low in Al₂O₃ and high in ZnO; an analysis gave ZnO 27.21, FeO 12.77, Fe₂O₃ 10.30, Al₂O₃ 50.55 per cent. At roasting temperatures Hamilton-Murray-McIntosh³ found that heating in a muffle pure Al₂O₃ and ZnO formed a compound insoluble in dilute H₂SO₄. Heating for 1 hr. to 853°C. rendered 82.2 per cent insoluble, for 3 hr. to 853°C.—85.30 per cent, and for 6 hr. to 630°C.—41.0 per cent. Aluminum silicates had no effect upon ZnO.

32. Zinc Ferrite, ZnFe₂O₄ (27.12 per cent Zn).⁴—This compound has been prepared by Ebelmen⁵ and Gorgen⁶ by heating a mixture of ZnO and Fe₂O₃. Ebelmen obtained black, brilliant octahedral crystals, which were a little harder than feldspar, slightly magnetic, had a specific gravity of 5.13, and formed a dark-brown powder which was insoluble in cold dilute HCl. The compound is found in some slags,⁷ but is formed mainly in dead-roasting iron-bearing blende. Its partial and total insolubility in leaching such blende with acids⁸ gave it technical interest. Hofman⁹ prepared it by heating ZnO with FeSO₄. Wells¹⁰ roasted in a muffle at temperatures reaching 800°C. mixtures of ZnS and FeS. By precipitating with NH₄S combined solutions of ZnSO₄ and FeSO₄, he found that as long as the ZnO content did not exceed the proportion ZnO:Fe₂O₃, and the temperature was sufficiently high, the ZnO became insoluble in Lowe solution (NH₄Cl, 200 gr.; NH₃, 500 c.c. (sp. gr. 0.90); H₂O, 750 c.c.); partly so in cold 10 per cent H₂SO₄; and readily in hot HCl (sp. gr. 1.10). In roasted iron-bearing blende, there is present a large excess of ZnO over that required to form ZnO·Fe₂O₃; it is held that basic ferrites, such as 2ZnO·Fe₂O₃ or 4ZnO·Fe₂O₃, are

¹ Percy, "Metallurgy," 1861, p. 539.

² Freiberg. Jahrb., 1881, p. 9; Berg. Hüttenm. Z., 1881, XL, 150.

³ Tr. Canad. Min. Inst., 1917, XX, 172.

⁴ Kohlmeier, Metallurgie, 1910, VII, 289.

⁵ Ann. chim. phys., 1851, XXXIII, 34.

⁶ Compt. rend., 1887, CIV, 580.

⁷ Hutchings, Eng. Min. J., 1903, LXXVI, 959.

⁸ Ingalls, Metallurgie, 1904, I, 334.

⁹ Tr. A. I. M. E., 1905, XXXV, 856.

¹⁰ Eng. Min. J., 1908, LXXXVI, 420.

formed which give up part of their ZnO to solvents. Thus Prost¹ dissolved with ammonium tartrate from roasted blende with 15.20 per cent Fe and 45.29 per cent Zn, 63.94 per cent Zn; from another sample with 1.50 per cent Fe and 62.86 per cent Zn, 95.42 per cent Zn; from a third sample with 5.28 per cent Fe and 57.80 per cent Zn, 74.67 per cent. The subject has been studied by Burleigh,² Lepiarczyk,³ Lindt,⁴ Brooks,⁵ and Hamilton-Murray-McIntosh.⁶ Brooks holds that the more intimate the contact of Zn and Fe (marmatite *vs.* ZnS + FeS) and the higher the temperature (a little below 1,000°C.), the greater is the amount of ferrite formed. Hamilton-Murray-McIntosh find that time and temperature aid the formation of ferrite. Working with Sullivan ore (Pb 13.2, Fe 25.3, SiO₂ 2.4, Al₂O₃ 2.9, CaO 1.4, S 28.5, Zn 22.6 per cent), of which 70 per cent passed through a 200-mesh screen, they obtained at 593°C. an extraction of 74.0 per cent Zn, at 649°, 76.1 per cent, when the yield fell with rise of temperature to 65 per cent at 815°C. In roasting blende preparatory to leaching with H₂SO₄ the temperature is held at 600° to 700°C. and air freely admitted (see also §126). Prost⁷ found that the ZnO in ZnO·Fe₂O₃ is completely reduced by C at a temperature of 1,100°C.

33. Zinc Sulphide, ZnS (67 per cent Zn; 65.37Zn + 32.06 S = 97.43ZnS + 43,000 cal.).—The existence of Zn₂S supposed by Bredberg⁸ does not seem probable, at least Friedrich⁹ failed to obtain it. The monosulphide occurs as blende. It is prepared in the dry way as a white powder by passing S or H₂S or CS₂ over heated Zn or ZnO, or by reducing ZnSO₄ with C at an elevated temperature; in wet way by precipitating with H₂S or NH₄S. Amorphous ZnS becomes crystalline by heating to a temperature approximating white heat, or about 1,200°C. Blende melts at about 1,650°C.;¹⁰ it is somewhat volatile at 1,000°C. Vogt¹¹ states volatility is noticeable only at 1,350°C.¹² It enters matte and reduces it fluidity.¹³

¹ *Bull. Assoc. Belge Chim.*, 1896, x, 246; *Min. Ind.*, 1896, v, 596.

² *Electrochem. Ind.*, 1904, II, 355.

³ *Metallurgie*, 1909, VI, 409.

⁴ *Op. cit.*, 1909, VI, 745.

⁵ *Tr. A. I. M. E.*, 1913, XLV, 210.

⁶ *Tr. Canad. Min. Inst.*, 1917, XX, 168.

⁷ *Bull. Assoc. Belge Chim.* 1896, x, 246.

⁸ *Pogg, Ann. Phys. Chem.*, 1829, XVII, 277.

⁹ *Metallurgie*, 1908, v, 593.

¹⁰ Vogt, "Die Sulfid: Silikat Schmelzlösungen," Kristiania, 1919, p. 3.

¹¹ *Loc. cit.*

¹² Doeltz-Graumann, *Metallurgie*, 1906, III, 442.

¹³ Hofman, "Lead," 1918, p. 392.

It is decomposed in the dry way by heating with access of air; roasting blende converts it into ZnO and SO₂ if temperatures are correct (details, see §50).

Heating with C has decomposing effect at a white heat: $2\text{ZnS} + \text{C} \rightleftharpoons \text{Zn}_2 + \text{CS}_2$; ¹ this has been verified by Fraenkel for 1,300°C. ² and by Prost for 1,450°C.; ³ Johnson ⁴ found that decomposition began at 1,200°C. and was satisfactory at 1,300°. The reaction is reversible at lower temperatures, ⁵ e.g. in a condenser, forming ZnS and soot which prevents zinc globules from coalescing. The reaction has no practical value as regards recovery of zinc. Lepiarczyk ⁶ suggests the reaction taking place is $\text{ZnS} + \text{C} = \text{Zn} + \text{CS}$, forming a volatile compound; or in case S is liberated, the reaction is $\text{ZnS} + n\text{C} = \text{Zn}_n \text{S}_{n-o} + \text{S}_o$; on the other hand, Fraenkel ⁷ believes that the vapors of C, Zn, and S react with SiO₂ present in the blende, reduce this to Si which combining with ZnS would form a volatile compound ZnS Si.

Iron readily decomposes ZnS at an elevated temperature. Prost ⁸ with a mixture of ZnS, Fe₂O₃ + C, using an excess of 20 per cent Fe, liberated at 1,200° to 1,250°C. 80 per cent of the zinc, and with an excess of 190 per cent Fe, all the zinc. Johnson ⁹ found that decomposition by Fe began at 1,167°C., and was complete at 1,250°; Graumann ¹⁰ obtained decomposition at 1,300°. The order in which Schütz ¹¹ placed some metals as regards their affinities for S is: Mn, Cu, Ni, Fe, Sn, Zn, Pb. Fe₂O₃ has a decomposing effect upon blende. According to Lepiarczyk ¹² the reaction $2\text{Fe}_2\text{O}_3 + 4\text{ZnS} = 3\text{FeS} + \text{Fe} + 4\text{ZnO} + \text{SO}_2$ takes place at 1,300° to 1,400°C., and in the presence of C the reaction is $\text{Fe}_2\text{O}_3 + 2\text{ZnS} + 4\text{C} = 2\text{Fe} + 2\text{Zn} + 3\text{CO} + \text{CS}_2$.

Lime.—Berthier ¹³ states that CaO acts upon ZnS only in the pres-

¹ Percy, "Metallurgy," 1861, p. 543.

² *Metallurgie*, 1909, VI, 682.

³ *Bull. Assoc. Belge. Chim.*, 1896, X, 246.

⁴ *Electrochem. Met. Ind.*, 1905, III, 15.

⁵ Lencauchez, *Mem. Soc. Ing. Civ.*, 1877, 672.

⁶ *Metallurgie*, 1909, VI, 409.

⁷ *Ibid.*, p. 682.

⁸ *Bull. Assoc. Belge. Chim.*, 1896, X, 246.

⁹ *Electrochem. Met. Ind.*, 1905, III, 15.

¹⁰ *Metallurgie*, 1907, IV, 77.

¹¹ *Op. cit.*, 1907, IV, 659, 694.

¹² *Op. cit.*, 1909, VI, 409.

¹³ "Traité des Essais," Thomine, Paris, 1834, II, 570.

ence of C; Percy¹ found that CaO acted in the absence of C; and Prost² decomposed ZnS completely at 1,250°C. using 75 per cent of CaO, and obtained the same result at 1,075° to 1,100° with 150 per cent excess CaO. Mostwitsch³ found that $\text{ZnS} + \text{CaO} + \text{N}$ did not react, but that in an atmosphere of CO there took place the reaction $\text{ZnS} + \text{CaO} + \text{CO} = \text{Zn} + \text{CaS} + \text{CO}_2$. Thus the presence of Fe and CaO may assist in the decomposition of ZnS in a charge of roasted blende.

Zinc Oxide.—According to Percy⁴ the reaction $\text{ZnS} + 2\text{ZnO} = 3\text{Zn} + \text{SO}_2$ takes place, if heating be prolonged sufficiently; otherwise oxysulphides ($\text{ZnS} \cdot \text{ZnO}$, $4\text{ZnS} \cdot \text{ZnO}$) are likely to form. The reaction of Percy is of no metallurgical importance.

Lead and Copper Oxides.—Litharge⁵ has a decomposing effect upon blende, forming Pb, ZnO, and SO_2 ; the ZnO is scorified by 25 times its weight of litharge. Cuprous oxide⁶ imperfectly decomposes ZnS, there is formed a coppery button and some matte.

*Tin, Lead, Antimony.*⁷—Percy⁷ tested the effects of these metals and obtained imperfect decompositions.

Hydrogen.—Berthier⁸ found that H did not act upon ZnS, but Morse⁹ obtained a decomposition with the formation of H_2S ; this gas acting with Zn vapor at a lower temperature formed again ZnS which was collected as a sublimate.

Water Vapor.—According to Thomas¹⁰ blende is partly decomposed at 650°C. in a current of water vapor according to the reaction $\text{ZnS} + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2\text{S}$. He substantiates the older research of Regnault.¹¹

Carbon Dioxide.—This gas was believed to have no effect on blende,¹² but Bacho¹³ found that prepared ZnS began to be attacked at 750°C., and rapidly decomposed at 900° to 1,000° according to $\text{ZnS} + 3\text{CO}_2 \rightarrow \text{ZnO} + \text{SO}_2 + 3\text{CO}$.

¹ "Metallurgy," 1861, p. 546.

² *Bull. Assoc. Belge. Chim.*, 1896, x, 264.

³ *Metallurgie*, 1911, VIII, 763.

⁴ *Op. cit.*, p. 54.

⁵ Berthier, *op. cit.*, I, 403.

⁶ Percy, *op. cit.*, p. 542.

⁷ *Op. cit.*, 543.

⁸ *Ann. Min.*, 1837, XI, 46.

⁹ *Chem. Zt.*, 1889, XIII, 79.

¹⁰ *Metallurgie*, 1910, VII, 610.

¹¹ *Ann. Min.*, 1837, XI, 46.

¹² Percy, *op. cit.*, p. 544.

¹³ *Monatshefte*, 1916, XXXVII, 119.

Manganese Dioxide.—This decomposes ZnS at a white heat,¹ forming ZnO, MnO, and SO₂.

Niter.—Niter readily decomposes blende² forming ZnO and SO₃, which remains in combination with the alkali base.

Alkali Carbonates.—These decompose³ ZnS at a red heat, CO₂ being set free but no metallic Zn. The product is a mixture of ZnO, ZnS, and Alk₂S, if the proportion 1Alk₂CO₃: 1ZnS is used; when the alkali sulphide contains more S than is required by the formula Alk₂S, some zinc is oxidized to ZnO by the CO₂ set free.

Acids and Caustic Alkali.—Of the acids, H₂SO₄ and HCl act slowly, HNO₃ more energetically; concentrated hot solutions of caustic alkali dissolve ZnS.

34. **Zinc Selenide and Telluride.**—Zinc Selenide, ZnSe (45.21 per cent Zn; 66.37 Zn + 79.2 Se = 145.57 ZnSe + 30,300 cal.). This does not occur as a mineral, it may be formed by heating Zn and Se, but is better prepared by conducting SeH over Zn at a red heat.⁴ It is an amorphous yellow powder. The investigation of Chikashige-Jurosawa⁵ shows that Zn and Se do not mix in the liquid, but can be made to combine to form ZnSe; this is brittle, bright-yellow, does not change at 1,100°C., and has a sp. gr. of 5.29. Zinc Telluride, ZnTe (33.89 per cent Zn; 66.37 Zn + 127.5 Te = 193.87 ZnTe + 31,000 cal.) is formed by heating the components.⁶ The freezing-point curve of Kobayashi⁷ shows a single pronounced maximum, ZnTe, with eutectic points close to the ordinates. The compound forms dark-red crystals melting at 1,238°C.; it has a sp. gr. of 5.54 at 13°C.

35. **Zinc Chloride, ZnCl₂** (47.95 per cent Zn; 66.37 Zn + 70.92 Cl₂ = 137.29 ZnCl₂ + 97,400 cal.; in dilute solution 113,000 cal.).—It is formed by conducting dry Cl gas through molten Zn⁸ or moistened Zn, through ZnO heated to redness, and by chloridizing roast of ZnS. It melts at 365°C.⁹ to a brown liquid, which solidifies to

¹ Berthier, *op. cit.*, II, 569.

² Percy, *op. cit.*, p. 545.

³ Berthier, *op. cit.* II, 545.

⁴ Margottet, *Compt. rend.*, 1877, LXXXIV, 1295.

⁵ Mem. College Science, Kyoto, 1917, II, 245, through *J. Inst. Met.*, 1918, XIX, 256.

⁶ Margottet, *Compt. rend.*, 1877, LXXXIV, 1293; 1887, CV, 1294.

⁷ *J. Inst. Met.*, 1911, VI, 336.

⁸ Grünauer, *Zi. anorg. Chemie*, 1904, XXXIX, 389.

⁹ Grünauer, *loc. cit.*

ZINC COMPOUNDS

a white porcelanic mass; is very hygroscopic,¹ small amounts of H_2O lower the melting point to a temperature ranging from 290° to 340°C . It boils at 730°C .;² is a good conductor of electricity when molten, its conductivity per cubic centimeter at 400°C . is 0.026 reciprocal ohm;³ is decomposed into Zn and Cl by electrolysis requiring an e.m.f. of 1.50 volt.⁴ In the wet way ZnCl_2 is prepared by dissolving Zn or ZnO in HCl and evaporating, and heating the $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ formed. It is difficult to remove the H_2O completely, since the salt is likely to split into HCl and basic chloride ($x \cdot \text{ZnO} \cdot y \cdot \text{ZnCl}_2 \cdot z \cdot \text{H}_2\text{O}$). Precipitation with milk of lime or magnesia throws down $\text{ZnCl}_2 + x \cdot \text{H}_2\text{O}$ with H_2ZnO_2 . The solubility of ZnCl_2 in H_2O ⁵ is given in Table 14.

TABLE 14.—SOLUBILITY OF ZnCl_2 IN H_2O

Temperature, degrees Centigrade	Stable form of salt	Per cent ZnCl_2
0.0	$\text{ZnCl}_2 + 3\text{H}_2\text{O}$	67.5
5.0	$\text{ZnCl}_2 + 3\text{H}_2\text{O}$	69.7
6.5	$\text{ZnCl}_2 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$	71.6
10.0	$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$	73.1
12.5	$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$	75.2
11.5	$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} + 1\text{H}_2\text{O}$	77.0
20.0	$\text{ZnCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	78.6
26.0	$\text{ZnCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O} + 1\text{H}_2\text{O}$	80.9
28.0	$\text{ZnCl}_2 \cdot 1\text{H}_2\text{O} + \text{ZnCl}_2$	81.3
40.0	ZnCl_2	81.9
60.0	ZnCl_2	83.0
80.0	ZnCl_2	84.4
100.0	ZnCl_2	86.0
262.0	ZnCl_2	100.0

¹ Mylius-Dietz, *Zt. anorg. Chemie.*, 1905, XLIV, 209.² Freyer-Meyer, *Ber. deutsch. chem. Gesellsch.*, 1892, XXV, 638.³ Schultze, *Zt. anorg. Chemie.*, 1894, XXII, 333.⁴ Lorenz, R., "Die Electrolyse geschmolzener Salze," Knapp, Halle, 1905, I, 133, III, 220, 246.⁵ Mylius-Dietz, *Zt. anorg. Chemie.*, 1905, XLIV, 217.

CHAPTER VI

ZINC ORES

36. Introduction.—The minerals which form the basis of ores are few in number. They may be classed as sulphides (blende, wurtzite), oxides (zincite, franklinite), silicates (willemite, calamine), carbonates (smithsonite, hydrozincite), and sulphates (goslarite). In addition may be mentioned cadmia, throat accretions of blast furnaces treating zinc-bearing iron ores.

37. Zinc Minerals.—Blende and Wurtzite (ZnS ; 67 per cent Zn, 33 per cent S). The mineral blende (sphalerite, jack, rosin-jack, blackjack) forms isometric, and wurtzite hexagonal crystals. Blende is the common sulphide; wurtzite is rather rare, it has been noted in some Missouri and foreign ores. According to Noeltting¹ many massive zinc sulphide deposits may be mixtures of blende and wurtzite. The ordinary blende contains little Fe and has a reddish-brown color (rosin blende); the higher the Fe-content, present as FeS , the darker the color; with 10 per cent or more Fe the color is dark-brown to black, and the mineral often goes by the names of black blende and marmatite. Sulphides of Fe, Cu, Cd, As, Sb, and Hg,² silver and gold minerals, as well as oxide of tin, are associated with blende; the Cd-content of blende in the United States ranges from 0.0 to 0.4 per cent; the occurrence of Ge, Ga, Ind, and Tl has been noted in §6. The gangue is mainly calcareous, but sometimes it is silicious. Blende ores are usually low-grade. Thus in the Central States in 1917 the crude ore contained about 3 per cent blende which was concentrated to a product assaying 58 per cent Zn or 87 per cent blende; frequently, however blende concentrates contain from 33 to 55 per cent Zn or 50 to 82 per cent blende. Analysis of pure and complex blende concentrates are given in Table 15.

38. Zincite, Franklinite, Willemite.—Zincite (ZnO ; 80.3 per cent Zn) is a deep-red to orange-yellow hexagonal mineral which contains about 5 per cent Mn. Franklinite ($(\text{Fe}, \text{Zn}, \text{Mn})\text{O}$ · (Fe

¹ *Zi. Kryst. und Min.*, 1890, XVII, 220.

² Juretzka, *Metall u. Erz.*, 1915, XII, 307; *Eng. Min. J.*, 1916, CII, 66.

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TABLE 15.—ANALYSES OF PURE AND COMPLEX BLENDE CONCENTRATES

Zn	Joplin, Mo.	Sheet Ground, Mo.	Albermarle, Va.	Oklahoma-Kansas District, average 1,000 car samples	Park City, Utah	Midvale, Utah	Romley, Colo.	Gem, Idaho	Butte, Mont.	Butte, Mont.	Bully Hill, Cal.	Australia
Zn.....	58.260	59.000	62.11	58.60	46.00	28.250	39.50	38.80	53.90	48.60	29.00	48.80
Cd.....	0.304	0.058									0.30	0.05
Pb.....	0.700	0.293		1.04	1.86	3.600	11.70	10.00	1.53	1.85	tr.	6.12
Cu.....	0.049	0.054			1.54	1.060	2.12		2.82	1.85	2.18	0.33
Fe.....	2.230	1.900	3.44	1.60	7.40	24.870	2.80	13.50	4.40	8.60	15.30	8.55
Mn.....	0.010	none			2.00		0.77				0.50	1.00
CaCO ₃	1.880	tr.										
CaO.....			0.05	0.00	4.00			1.70	0.75	1.88	2.31	0.50
MgCO ₃		none										
MgO.....	0.850		none		tr.						2.86	0.06
BaSO ₄	0.820	tr.									2.92	
SiO ₂	3.950	0.971	0.26	5.20	4.10		14.10	8.50	3.60	3.60	6.30	1.75
NiCo.....	none	tr.										tr.
S.....	30.420	31.301	34.45	31.28	30.40		27.20	10.30			31.10	27.30
As.....					0.52				0.55	0.40		0.04
Sb.....												0.08
Al ₂ O ₃					5.20			5.90	3.60	8.60	8.26	0.56
Ag*.....						18.450			10.04	10.08		
Au*.....						0.015			0.04	0.08		
Reference.....	1	1	2	3	4	4	4	4	4	4	5	5

* Ounces per ton.

1. Waring, *Tr. A. I. M. E.* 1917, LVII, 662.
2. Watson, *Tr. A. I. M. E.* 1906, XXXVI, 688.
3. Johnson Heinz, *Eng. Min. J.* 1919, CVII, 558.
4. Lyon, D. A. RALSTON, O. C., Bull. 168, Bureau of Mines, 1919, p. 22.
5. Hansen, *Tr. A. I. M. E.*, 1919, LX, 208.

Mn)₂O₃ with 6 to 18 per cent Zn) is iron black, forms rounded octahedral crystals, is sufficiently magnetic to permit magnetic separation from zincite and willemite; the concentrate contains 30 to 47 per cent Fe, 10 to 19 per cent Mn, and about 22 per cent Zn. Willemite (Zn₂SiO₄, 58.61 per cent Zn) is apple-green, forms hexagonal prisms which contain 1.5 to 3.0 per cent Mn. The three minerals occur in Cambrian limestone in New Jersey. The two leading mines worked by the New Jersey Zinc Co. are at Franklin Furnace and Stirling Hill. The ore as mined contains 19 to 22 per cent Fe, 6 to 12 per cent Mn, and 27 per cent Zn. It is subjected to wet concentration to recover zincite and willemite, and to magnetic concentration to enrich the franklinite. The latter process furnishes¹ franklinite (Zn 18.2, Fe 35.0, Mn 12.8, SiO₂ 3.6 per cent), half and half (Zn 18.4, Fe 15.2, Mn 2.2, SiO₂ 12.6 per cent) and dust (Zn 17.6, Fe 20.1, Mn 8.9, SiO₂ 7.2 per cent); the franklinite is worked for zinc oxide (§140), the other two products are first mixed.

39. Calamine, Smithsonite, Hydrozincite.—Calamine (2ZnSiO₂ + H₂O, 57.1 per cent Zn) is a white mineral having a bluish to greenish shade which forms ortho-rhombic crystals, and has a vitreous luster. Smithsonite (ZnCO₃, 52.14 per cent Zn) is also white, but often grayish or greenish, forms curved imperfect rhombohedral crystals, it occurs frequently in crystalline incrustations.² Hydro-

TABLE 16.—ANALYSES OF OXIDE ORES

	Joplin, Mo. concentrate		Falling Creek, Va.		Joplin, Mo. concentrate		Falling Creek, Va.
Zn, total.....	57.30	51.80		SiO ₂	..	..	24.47
Zn as ZnS.....	18.20	8.65		Fe ₂ O ₃	..	..	2.10
Zn as Zn ₂ SiO ₄ +				Al ₂ O ₃	..	..	1.24
H ₂ O.....	33.10	43.15		Mn ₂ O ₃	..	..	0.16
Fe.....	1.50	1.30		ZnO.....	..	..	61.84
CaO.....	0.42	0.40	0.53	CO ₂	..	..	1.80
MgO.....			0.21	H ₂ O.....	..	..	8.27
Pb.....	None	None		Reference...	I	I	2.00

1. Waring, *Tr. A. I. M. E.*, 1917, LVII, 661.

2. Dewey, *op cit.*, 1882, X, 112.

¹ Stone, *Tr. A. I. M. E.*, 1917, LVII, 682.

² In English technical literature the meanings of the names calamine and smithsonite are reversed.

zincite ($3\text{ZnCO}_3 \cdot 2\text{H}_2\text{O}$, 47.58 per cent Zn) forms earthy to compact white to yellowish incrustations, is sometimes reniform or stalactitic. The three minerals occur together in oxide zones of deposits, and go to form the so-called carbonate ores. Calamine is very common; smithsonite is rare in the United States, but important in Europe. Both are likely to be impure, and found as incrustations which have an earthy character rather than a crystalline form. Hydrozincite is not uncommon. Table 16 gives analyses of oxide ores.

40. Goslarite and Cadmia.—Goslarite ($\text{ZnSO}_4 + 7\text{H}_2\text{O}$, 22.65 per cent Zn) forms white vitreous ortho-rhombic crystals. It is a secondary mineral, massive or stalactitic, resulting from the alteration of blende, but is of little importance as an ore.

Cadmia is an impure oxide of zinc forming throat accretions in iron blast furnaces treating zincky ores. Table 17 shows the composition of cadmia from Virginia where zinc-bearing gossan furnished the iron ore.

TABLE 17.—ANALYSES OF CADMIA

	Longdale, Va.	Low Moor, Va.
SiO_2	0.94	2.410
Fe.....	2.44	
FeO.....		1.270
PbO.....	0.90	
MnO ₂		3.600
CaO.....	1.22	1.850
ZnO.....	93.89	87.660
C, loss.....	0.61	0.640
Al ₂ O ₃		0.228
P ₂ O ₅		0.701
SO ₃		0.493
Total.....	100.00	98.852
Reference.....	1	2

1 Firmstone, *Tr. A. I. M. E.*, 1879, VII, 97.

2 Means, *op. cit.*, 1888-89, XVII, 130.

41. Zinc Ores of the United States.—The relative importance of the several states as producers of zinc ores has been shown in Table 2. In reviewing the districts, it is convenient to group them under headings of Eastern Central and Western.

42. Eastern District.—The principal producer is in the Franklin Furnace region of New Jersey with its two leading mines Sterling Hill and Mine Hill. These form synclinal folds in white paleozoic limestone bounded by gneiss and blue Cambrian limestone. The leading ore minerals are franklinite, willemite, and zincite; the gangue minerals are calcite, rhodonite, garnet, pyroxene, and hornblende; Sterling Hill contains in addition tephroite, and Mine Hill silicates of manganese and zinc. There is gradation from ore into country rock. The spelter produced is high grade, being free from the usual impurities Pb, Cd, and Cu.

The Virginia-Tennessee area is the only other zinc-producing region. The deposits occur in a belt of Cambrian limestone extending from southwest Virginia into eastern Tennessee. In Virginia there have been mined mainly weathered ores, with calamine, smithsonite, and cerrusite as metal-bearing minerals; they are found in residual clays surrounding pinnacles (chimneys) of limestone, and are concentrated to a product with 40 per cent Zn. The Bertha and Austinville mines have been the chief producers; Bertha zinc is known for its purity: Zn 99.90, Fe and Pb 0.10 per cent. In the limestone occur primary ores containing blende, galena, and pyrite, which form irregular masses in brecciated rock. The gangue minerals are calcite and dolomite with some barite; fluorite and chert are not uncommon. These ores are of growing importance.

In Tennessee zinc ores are more abundant than lead ores; they are found mainly in brecciated areas of dolomitic limestone which adjoin fault zones. Both oxide and sulphide ores are produced, some are lead-bearing, others are not. The ores of the Mascot mines contain 8 to 10 per cent blende, no Fe, no Pb; wet concentration furnishes a market product with Zn 59 to 61 per cent, Fe under 1 per cent, Pb usually under 0.01 per cent. Carbonate ores contain Zn 30 to 40 per cent. The brand of spelter named Mascot, is highgrade.

43. Central District.—This embraces the Upper Mississippi Valley, the Ozark region, and outlying areas of northern Arkansas, Kentucky, and Illinois.

The Upper Mississippi Valley region includes southwestern Wisconsin, eastern Iowa, and northwestern Illinois. Of these, Wisconsin is the leader. The ores occur in the galena dolomite and the upper part of the Plattesville limestone, both of Ordovician age. They are found in crevices and as disseminations; galena predominates in vertical crevices, blende is found lower down in flats which are

horizontal branches of the crevices. Calcite is the common gangue mineral. In some mines marcasite is so plentiful that the blende concentrate runs low in zinc, and has to be cleaned by a superficial (flash) roast,¹ followed by magnetic concentration. The raw ores contain 8 to 14 per cent blende and an equal amount of marcasite; wet concentration gives an intermediary product with Zn 30, Fe 25, CaO 4-5, SiO₂ 2-3 per cent; flash roast followed by magnetic concentration gives a market product with Zn 58 to 60, Fe 2 to 4, CaO 0.7 to 1.4, SiO₂ 1 to 2 per cent. Above waterlevel the blende has been changed to smithsonite (dry bone). Blende is the main product. The ores of eastern Iowa and northwestern Illinois are similar to those of Wisconsin.

The Ozark region lies mainly in Missouri, but includes portions of Arkansas and Oklahoma. The ores are found in southwestern and central Missouri, northwestern Arkansas, and northeastern Oklahoma. The principal district is the southwestern or Missouri-Kansas-Oklahoma district, of which the Joplin area is the center. The ore is found in carboniferous limestone and chert, which are brecciated and cemented by dolomite, calcite and blende, and carry blende, galena, and marcasite. In addition there occur chalcopyrite, greenockite, barite and other minerals. Above water level are found oxides and silicates. The ore-bodies form *runs* and *sheet ground*. Runs are irregular tabular ore-bodies, 10 to 50 ft. wide and comparatively shallow; sheet ground has a similar form but is of great lateral extent and from 15 to 16 ft. thick. An ore-body with 6 per cent Zn is considered as valuable. Water and magnetic concentration furnish a concentrate (jack) with 58 per cent Zn. The ores of central Missouri, Arkansas, Kentucky and southern Illinois are of less importance than the preceding.

44. Western District.—The leading states producing zinc ore are New Mexico, Colorado, Montana, Idaho, Utah, Arizona, Nevada and California.

In New Mexico zinc ores are mined mainly in the northwestern part of the state. In the Magdalena range, near the town of Kelly, blende occurs in veins and bed replacements close to fault fissures in carboniferous limestones, quartzites and shales cut by monzonite; replacements are of more importance than veins. The gangue minerals are pyrite, magnetite, hematite, quartz, barite, galena, and blende; the blende is dark and contains considerable amounts of iron. The raw ore contains Zn 18, and Pb 4 to 6 per cent, a little

¹Hofman-Norton, *Tr. A. I. M. E.*, 1905, xxxv, 928.

Ag and Au; it is concentrated to a product with Zn 45 per cent. Rich crude ore is shipped to oxide plants.

In Colorado the zinc deposits occur mainly in a belt extending from the Rico district in the San Juan region northeasterly to the Central district in Boulder County. In the Leadville region the most important deposits are found in Carboniferous limestone, they lie against the white porphyry above and extend irregularly into the limestone below. Zinc carbonate and silicate are found below the carbonate lead deposits. In the undecomposed zones the ores consist of about equal quantities of galena, blende, and pyrite. Table 18 gives works analyses of ores received at smelteries.

TABLE 18.—ANALYSES OF COLORADO ZINC ORES

	Au	Ag	Pb	Cu	Insol.	Fe	CaO	S	Zn
Carbonate ore.....	...	3.0	6.0	...	15.0	7.0	2.5	3.0	30.0
Carbonate ore.....	tr.	5.0	5.0	...	16.0	3.0	8.0		32.0
Carbonate ore.....	tr.	6.0	8.0	...	10.0	6.0	5.0		32.0
Sulphide ore.....	tr.	6.0	9.0	...	16.0	14.0	1.0	21.0	24.0
Sulphide ore.....	tr.	10.0	6.0	6.0	8.0	13.0	4.0	26.0	30.0
Sulphide ore.....	0.45	9.0	6.0	1.0	20.0	16.0	...	22.0	35.0
Sulphide ore.....	0.30	25.0	6.0	...	10.5	15.0	0.5	28.0	40.0
Sulphide ore.....	0.02	20.0	3.0	0.5	9.0	3.0	...	29.0	52.0

Montana.—The mining is centered in the Butte district. The ores are replacement veins in quartz, monzonite, aplite, and porphyry. The ore comes mainly from mines formerly operated as silver producers, but abandoned an account of the low price of silver. The Black Rock mine, worked by the Butte and Superior Mining Co., is the leading producer. The crude ore contains Zn 16 to 17, Pb, Cu 0.7 per cent, Ag 7 oz. per ton, Au a little; the concentrate, Zn 52, Pb 6.2, Fe 4 per cent, Ag 22 oz. per ton, Au a little. Usual wet concentration yielded only 55 per cent of the Zn content; supplemented by flotation the recovery has been increased to 93 and 95 per cent. The flotation concentrates are difficult to roast in kilns owing to their fineness. The ore and product of the Elm Osler mine are similar to that of the Black Rock mine. The old silver mines, such as the celebrated Alice, Lexington, Emma, etc., are being developed. Their raw ores will average Zn 13 to 15, Pb 3 to 5, Cu 1 per cent, Ag 3 to 5 oz. per ton, Au a little; the concentrates, Zn 30 to 40, Pb 3 to 4, Cu 2 per cent, Ag 10 oz. per ton, Au a little.

Idaho.—Blende and blende with galena are mined in the Coeur d'Alene district in which they form fissure veins which penetrate Algonkian sedimentary rocks, such as quartzite, shale, and schist. The ores are rich sulphides and silver-bearing, they are concentrated to blende, galena, and intermediaries which are subjected to a sulphatizing roast and lixiviation; the zinc is recovered from solution by electrodeposition, and the lead in the residue by smelting. Flotation concentrates contain Zn 35 to 45 per cent and some precious metal. The mines of the Interstate Callahan Mining Co. of Coeur d'Alene (changed to Callahan Zinc-Lead Co.) have zinc-lead ores which furnish a blende concentrate with Zn 50, Pb 5 per cent, Ag 3 to 4 oz. per ton, and a little Au.

Utah.—At first (1904) only blende was mined, but in recent years there has been a considerable output of oxide ore. The ore-bodies in the Park City region (Daly-Judge and Daly-West mines) are replacements of limestones adjacent fissure veins which penetrate folded limestones, quartzites, and shales from Carboniferous to Triassic age. The ores carry silver, concentrates assay Zn 40 to 45 per cent, and Ag 10 to 25 oz. per ton. In the Tintic district the ores occur in a manner similar to that of Park City, in addition they form veins in a monzonite intrusive. The ores in the limestone are largely oxidized.

Arizona.—The principal producers, the Golconda (recently shut down) and Tennessee mines, lie in Mohave County. The ore occurs in fissure veins, and carries galena and blende, also Ag, several dollars in Au, and some Cu; the blende is dark, carrying considerable amounts of Fe. Tennessee concentrates contain Zn 30 to 45 per cent.

Nevada.—Most of the zinc ores come from Yellow Pine district in Clark County. The rocks of the region are limestone, sandstone and shale which have been much folded and faulted, and penetrated by granite porphyry and quartz monzonite. The ore-bodies are replacements of limestone near fissure veins; the minerals are zinc carbonate and silicate. The ores with Zn 32, Pb 10 per cent, and 5 oz. Ag per ton, are concentrated; the zinc concentrate assays Zn 30 to 40, Pb 10 to 12, it is shipped to oxide plants.

California.—In Shasta County blende is associated with sulphide copper ore in ore-bodies resulting from replacement of country rock (alaskite, porphyry) along shear zones; the gangue minerals are quartzite, calcite, and barite. Crude Mammoth ore contains Zn 30 to 35 per cent. The ore is smelted pyritically for matte,

while the zinc is volatilized; the gases are filtered, and the fumes treated electrolytically. Ore from the Afterthought mine contains Zn 15 to 20, Cu 1 to 2, a little Pb, Ag and Au; an electrolytic process is contemplated. In Inyo County oxide ores with galena and cerussite occur as replacements in limestones; they are believed to be genetically related to an intrusive mass of monzonite porphyry. The shipments of oxide average Zn 30 to 40 per cent.

45. Marketing Zinc Ores.¹—The leading requirement of a zinc smeltery is that it commands an abundant supply of fuel at a low price, hence smelting-ore is always treated in a custom plant. European plants in Belgium, England, and Germany have adopted formulas for calculating the prices to be paid for zinc ores. Such a formula is

$$V = 0.95P \left(\frac{T - 8}{100} \right) - S$$

in which V = value of ore per ton of 2,240 lb. at ship, Antwerp, Swansea, or Hamburg; P = average price of spelter (Good Ordinary Brand) at London during the month of delivery of ore given in francs, pounds sterling, marks, or dollars according as P , the value of spelter in London, is reckoned in francs, pounds sterling, marks, or dollars; T = the percentage of zinc in the ore as shown by assay; S = the returning charge.

The first item, $0.95P$, represents a 5 per cent deduction from the quotation; $T - 8$ covers the loss in smelting, it increases as the tenor in zinc decreases; the returning charge, S , includes carriage of ore from seaport to works, the cost of smelting, and the profit of the smeltery. The cost of smelting will vary considerably with the character of the ore (sulphide, oxide), the presence or absence of impurities (Fe, Mn, CaO; Pb, Cd, As, Sb; CaF_2), the physical character (coarse, medium, fine), and the reducibility.

In the Joplin district of Missouri² the method of purchasing is

¹ Ingalls, W. R., "Production and Properties of Zinc," McGraw-Hill Book Co., Inc., New York, 1902, p. 303.

Smith, E. A., "The Zinc Industry," Longmans Greene, & Co., London, 1918, p. 70.

Waring, *Eng. Min. J.*, 1900, LXX, 38.

Ingalls, W. R., "Report of Commission, Zinc Resources, British Columbia," Mines Branch, Dep't. of Interior, Ottawa, 1906, p. 22.

Martin, *Min. Ind.*, 1907, XVI, 930; *Eng. Min. J.*, 1908, LXXXV, 803.

Wittich, *Mines and Minerals*, 1911, XXXI, 550.

Editor, *Eng. Min. J.*, 1917, CII, 781.

² Waring, *Eng. Min. J.*, 1900, LXX, 38.

the following. There are deducted 50 cts. per ton for each per cent of Pb in the ore, and \$1 per ton for each per cent of Fe in excess of 1 per cent. The smelting charge, which includes commissions, freight and cost of smelting, is assumed to be \$10.50 per ton of ore. To this is added a margin of profit varying from \$4 to \$8 per ton when spelter is quoted at St. Louis at 4 cts. per pound or from \$6 to \$12 per ton when the quotation is 6 cts. per pound. The nominal cost of \$10.50 applies equally to low- and high-grade ores, but the margin of profit is increased with low-grade ores to cover the extra loss and cost of treatment. The formula applied by the leading smelteries is

$$V = W.Q - (E + P)$$

in which

W = 80 per cent of the number of pounds of zinc contained in a net ton of dry ore as found by assay; if the assay be A , then $W = 16A$ instead of $20A$.

Q = St. Louis spelter quotation per pound at time of purchase.

E = expense: freight and cost of treatment (\$10.50).

P = smelter's profit, etc. = $100Q$ when $A = 60$ per cent and over; $P = 100Q + (10Q \times 60 - A)$, when A is less than 60 per cent.

V = value of ore at mine, subject to deductions for Fe and Pb contents allowing 20 per cent Zn for loss; the total smelting charges upon ore with 60 to 65 per cent Zn vary from \$13.50 to \$16.50 per ton, and upon ore with 50 per cent Zn from \$16.50 to \$22.50 per ton, according as the price of spelter varies from 3 to 6 cts. per pound. In 1918¹ new schedules were proposed, but they failed of general adoption.

46. Metallurgical Treatment in General.—Zinc is extracted from its ores almost exclusively by smelting, and sold as spelter. Leaching (§123) has found application with mixed ores after these have been given a preparatory treatment to render them amenable to solvents. From the solutions, the zinc salt may be recovered as such ($ZnSO_4$, $ZnCl_2$), or zinc compounds (ZnO) precipitated chemically, which require further treatment; electro deposition (§123) has become an established process in recent years. The residue from leached ore, freed from most of the zinc, can now be smelted for its base and precious metals. Beside spelter there is produced from oxide and roasted ore pure and leaded zinc oxide as a market product by the Wetherill process (§139).

¹ *Eng. Min. J.*, 1918, CVI, 791.

47. Location of Smelting Plant; Cost; Sanitation.—The location of a zinc smelter¹ is largely governed by the character and cheapness of the fuel. Laur² stated over 40 years ago that in order to produce 1 ton of spelter, there were required 3 tons ore, 5 to 6 tons coal, 0.35 refractory material, and a dumping space for 6 tons or 6m.³(= 212.6 cu. ft.) ashes and refuse. In our days, at least in the United States, 2.5 tons ore for 1 ton of spelter is a better average than 3; the ratio of 1 ton ore to 2 tons coal remains true in most cases, in some instances,³ however, the ratio of 1 : 1 has been reached; the dumping space has to hold for 1 ton of ore 0.5 to 1.0 ton of refuse which at 50 lb. per cubic foot would require from 20 to 40, average 30 cu. ft. space. Zinc smelteries are best erected on level ground which has a sharp declivity to provide room for an extended dump.

The cost of plant⁴ using coal as fuel is about \$16 per ton of ore, and \$10 if natural gas is the heating fuel, the difference being caused by the cost of regenerative chambers, gas producers, boilers, and the means of storing and handling large quantities of coal. The figures, given in 1906, are for a plant treating 25,000 tons of ore per year; the cost of smaller plants is proportionally higher. The figures do not include the acid plant which⁵ before the war would cost \$15 per annual ton of smelting capacity. The above estimates would have to be increased perhaps by 50 and even 100 per cent to meet present conditions.

The place of a zinc plant is therefore near the supply of fuel; it ought not to be too distant from the source of refractory material, and must have an abundance of water. The ore is shipped to the smelter. In many instances it is roasted on its way from the mine to the smelter in places which are suited for the manufacture of sulphuric acid. There have to be considered the disposition of SO₂ gases in case reverberatory furnaces are used for roasting, and of zinc fumes which are likely to cause complaint and be a cause of

¹ Juretzka, *Metall. u. Erz.*, 1913, X, 123, 125, 129, 161.

² *Bull. Ind. Minérale*, 1874, III, 395; *Eng. Min. J.*, 1875, XX, 406; *Berg. Hüttenm. Z.*, XXV, 6, 1876.

³ Ingalls, *Eng. Min. J.*, 1919, CVII, 87; Choate, *Chem. Met. Eng.*, 1919, XX, 237.

⁴ Ingalls, W. R., "Report of Zinc Commission," Mines Branch, Dep't. of Interior, Ottawa, 1906, p. 31.

⁵ Wilson, A. W. G., "Report on the Production of Spelter in Canada," Ottawa, 1916, p. 3.

ts for damages.¹ Drawings and descriptions of some of the recent zinc smelteries are referred to in the footnote.² tary arrangements have to be provided to remove the fumes ne furnace and buildings.³

fumes⁴ inhaled have a harmful effect in that they cause le, nausea, weakness, and chills (spelter shakes). Some of ects are similar to those of lead⁵ and may be caused by the ce of this metal, others (brass ague) have been attributed to .⁶

tor, *Rauch u. Staub.*, 1912-13, III, 200.

. *Min. J.*: Walker, 1907, LXXXIV, 161 Vivian & Sons, South Wales; 1909, LVXXX, 777, Central Zinc Co., Seaton Carew, England; Buskett, C, 502, Am. Zinc, Lead & Smelting Co., Deering, Kan; Ingalls, 1914, 985, Am. Zinc & Chemical Co., Langeloth, Pa.; Ingalls, 1916, CII, 648, eel & Wire Co., Donora, Pa.; Bocking, 1916, CI, 655, Arkansas Zinc & ig Co., Van Buren, Ark.; Ingalls, 1917, CIII, 832, Judge Mining & Smelt- . (electrolysis).

ing & Scientific Press: Leslie, 1914, CIX, 204, Bartlesville Zinc Co.; Collins- Okla; 1914, CIX, 137, National Zinc Co., Bartlesville, Okla.; 1914, CIX, m. Zinc, Lead & Smelting Co., Hillsboro, Ill.; 1914, CIX, 395, Granby & Smelting Co., Rose Lake, Mo.; 1914, CIX, 475, Nassau Zinc Works, , Ill.; 1914, CIX, 44, Lanyon Starr Smelting Co., Bartlesville, Okla.

Age: Editor, 1916, XCVII, 82, Am. Steel & Wire Co., Donora, Pa.

ing World: Breger, 1912, XXXVIII, 847, Am. Zinc, Lead & Smelting Co., oro, Ill.

mieder, *Oest. Zt. Berg. Hüttenw.*, 1890, XXXVIII, 459; *Berg. Hüttenm. Z.*, CLIX, 301.

m, *Berg. Hüttenm. Z.*, 1892, LI, 344.

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sling, *Berg. Hüttenm. Z.*, 1902, LXI, 478; *Min. Ind.*, 1902, XI, 614.

lson, *Metall. u. Erz.*, 1913, X, 257.

vs in Prussia, *op. cit.*, 1914, XI, 1.

old, *op. cit.*, 1915, XII, 403, 419.

ffert, *Eng. Min. J.*, 1897, LXIV, 579.

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mer, *loc. cit.*

ton, *Eng. Min. J.*, 1915, C, 363.

nson, *op. cit.*, 1915, C, 1016.

frman, "Lead," 1918, p. 637.

nsen, *Met. Chem. Eng.*, 1911, IX, 67.

CHAPTER VII

SMELTING OF ZINC ORES

48. Introduction—The minerals forming zinc ores (§37) are blende or carbonates and silicates. As zinc oxide, including some silicate, forms the basal compound from which spelter is produced by means of smelting, anhydrous and hydrous carbonates as well as hydrous silicates have to be freed from their volatile constituents by calcining, and blende has to be converted into oxide by roasting.

Electrothermic processes attempting to treat raw and roasted blende are noted in §121, and electrolytic processes in §123.

Zinc oxide, to be reduced to zinc by C, requires that an intimate mixture of the two be heated to $1,100^{\circ}\text{C}$; zinc silicates demand a higher temperature than zinc oxide. As the boiling point of zinc lies at 920°C ., the reduced zinc is in the state of vapor. The vapor has to be protected from the oxidizing action of O (air), H_2O -vapor, and CO_2 , hence, reduction must be carried on in a closed vessel in the presence of an excess of C. Beside C, the gas CO may act as a reducing agent forming CO_2 , but this is at once reduced again to CO by C; CO therefore forms an intermediary between ZnO and C supplementing the imperfect intimate contact between the two solids. The vapor has to be condensed at a temperature lying above 419°C ., the melting point of Zn, if liquid zinc is to be obtained, and below 550°C ., at which temperature the vapor pressure¹ of zinc is only 4.38 mm. Hg, if condensation is to be satisfactory. The condenser is a clay receiver attached to the closed vessel. If condensation takes place below 419°C ., *i.e.*, if the condenser is too cool, the zinc vapor solidifies in a finely-divided state forming so-called blue powder; this will also occur if the zinc vapor is diluted by non-oxidizing gases, such as N, CO, CH_4 . Blue powder will always form when a new charge is being

¹ Richards, J. W., "Metallurgical Calculations," McGraw-Hill Book Co., Inc., New York, 1918, p. 645.

heated up, as the condenser will always be too cool, and the reducing fuel giving off its volatile constituents will dilute the zinc vapor. The usual smelting process, which is carried on in various forms of closed vessels of small capacity made of fireclay, suffers from a loss of zinc which exceeds 10 per cent; from a high cost of treatment, caused by the expense and short life of the closed vessel and the low thermal efficiency (2 to 5 per cent) of closed-vessel furnaces; from the smallness of the charge; and the requirement of ores rich in zinc. Low-grade ores have to be enriched by water-concentration, magnetic or electrostatic processes, or by a volatilization roast which furnishes oxide (§71). Many attempts have been made to substitute the blast furnace (§118) for the retort, but they have proved failures; electric and electrolytic processes have been noted above. By whatever process metallic zinc is obtained, the crude metal has to be refined, usually by liquation, that it may meet the requirements of the metal industries.

CALCINING AND ROASTING

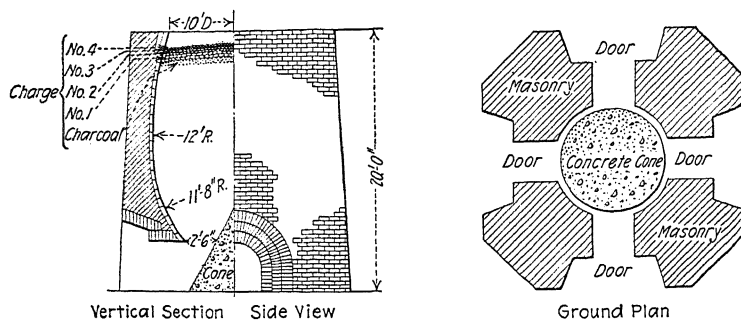
49. Calcination of Oxide Ore.—The object of calcining oxide ores is to drive off CO_2 and H_2O , and to disintegrate the ore. If CO_2 and H_2O are not eliminated before smelting, they will have to be expelled in the retort, which is expensive and may cause oxidation of zinc vapor. Disintegration facilitates hand-sorting of impure ores and subsequent reduction in the retort. Leaving out of consideration, zincite, willemite and franklinite, oxide ores contain smithsonite (35.2 per cent CO_2), hydrozincite (13.6 per cent CO_2 , 11.1 per cent H_2O), and calamine (7.5 per cent H_2O) as zinc minerals; the gangue minerals which lose a volatile constituent upon heating are carbonates of lead, iron, magnesium and calcium. The zinc minerals give up CO_2 and H_2O at about 400°C ., the gangue minerals their CO_2 at temperatures ranging from 300° to 800°C . In calcining, oxide ores lose 20 to 30 per cent in weight. In account of the opportunity for hand-sorting and the reduction in weight, calcining may be carried on at the mine. However, in calcined ore the ZnO is likely to take up again some CO_2 ,¹ and CaO in addition some H_2O and to become slaked; hence, calcined ore ought not be stored. In calcining calcareous ores it is not advisable to expel all the CO_2 , as they lose zinc owing to reduction of ZnO .²

¹ Doeltz-Graumann, *Metallurgie*, 1906, III, 443.

² Steger, *Berg. Hüttenm. Z.*, 1886, XLV, 353.

Thus at Rosdzin, Upper Silesia, only the H_2O is driven off, and the calcined ore with 7.81 per cent CO_2 charged into the muffle; at the Hohenlohe works¹ raw fines are charged with calcined lump ore and roasted blende; our Western smelteries² follow a similar procedure.

The furnaces are kilns (continuous shaft furnaces) for lump ore which contain not over 15 to 20 per cent fines, and reverberatory



FIGS. 16 and 17.—Calcining kiln for oxide zinc ore.

furnaces for fines. In shaft furnaces ore and fuel are charged in alternate horizontal layers, or the ore is charged alone and the shaft heated from external fireplaces; the waste of the gases from distilling furnaces has served for this purpose, but other methods of utilizing this heat are more advantageous. Charging ore and 4 to 6 per cent fuel together is simple and cheap, but it has the disadvantage that some ZnO is liable to be reduced and lost, and that the ores become contaminated with the ashes of the fuel which are likely to be S-bearing unless charcoal is used.

A kiln to be charged with ore and fuel is shown in Figs. 16 and 17. It resembles an ordinary lime kiln, built of stone and lined with brick; the plan is a hexagon 16 ft. in diameter, the elevation shows a shaft 20 ft. high, 10 ft. in diameter at the throat, bellied out to 12 ft. to allow for expansion of ore, contracted down to 11 ft. 8 in., and ending in four discharge openings 2 ft. 6 in. wide. In the center is a concrete cone, 8 ft. in diameter and 5 ft. high, covered with sheet

¹ Schmieder, *Oest. Jahrb.*, 1889, XXXVII, 401; *Berg. Hüttenm. Z.*, 1890, XLIX, 130.

² Simpson, *Met. Chem. Eng.*, 1916, XIV, 181.

iron. The ore is screened into four sizes: 4, 2, 1 and $\frac{1}{4}$ in. in diameter. In starting, the kiln is filled with wood to a point above the discharging doors, then follow in succession 4-in., 2-in., 1-in. and $\frac{1}{4}$ -in. layers of ore; on top of this comes a layer of charcoal or coal about 4 per cent of the weight of a charge, to be followed by a layer of ore as indicated. A charge is made up of 28 barrows of ore (5b.-4 in., 5b.-2 in., 2b.-1 in., 1b.- $\frac{1}{4}$ in.), each weighing about 400 lb., or 11,200 lb. in all and 450 lb. charcoal. The furnace, filled to about 1 ft. below the feed floor, holds from 8 to 10 charges. The wood on the bottom is kindled and furnishes the heat necessary for igniting the charcoal or coal of the charge. At intervals of about 6 hr. a given quantity of calcined ore is withdrawn at the bottom, and a corresponding amount of new charge fed at the top; 70 tons calcined ore equal 90 tons raw ore. Imperfectly calcined ore is returned to the furnace. The furnace treats in 24 hr. from 25 to 46 tons raw ore and furnishes from 20 to 36 tons calcined ore. The cost is two-thirds that of burning limestone, which requires about 15 per cent of coal. Burning limestone costs about \$1 per ton of limestone with coal at \$6 per ton. The furnace shown in Figs. 16 and 17 is a clumsy structure; at present a furnace would be modeled on the form of an iron blast furnace, that is, a collar supported by structural-steel or cast-iron legs would carry a sheathed shaft. The furnace has also the disadvantage that the calcined ore has to be shoveled into cars.

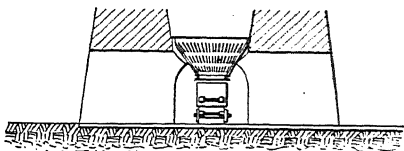


FIG. 18.—Ferrate calcining kiln with grate.

The Ferrari furnace at Monteponi, Sardinia,¹ does away with shoveling in that it has, Fig. 18, a hopper-shaped perforated cast-iron grate suspended from a horizontal cast-iron ring let into the side wall. The grate is made up of eight sections and is closed at the bottom by five wrought-iron bars. The ore is charged with 4 to 6 per cent charcoal fines and discharged into a car beneath by shaking and turning the bars; when necessary, wrought-iron bars are passed through the upper part of the grate, the lower bars are withdrawn, and the calcined ore between them dropped. The conical furnace is 26 ft. 3 in. high, 5 ft. 6 in. in diameter at the throat and 6 ft. 6 in. at the top of the grate; the conical grate is 3 ft. 3 in. in diameter at the bottom, and about 3 ft. high.

¹ *Oest. Zt. Berg. Hüttenw.*, 1886, xxxiv, 655.

Coarse-ore furnaces with external fireplaces permit a more careful regulation of temperature than when ore and fuel are charged together, and avoid mixing of coal ashes and ore. Such a furnace with one fireplace, in operation in Spain about 1860, is shown in

Figs. 19 and 20. It furnished¹ in 24 hr. 5 to 8 tons calcined ore, required 8 to 9 per cent coal and 6 men. A furnace with two fireplaces furnished 10 tons product with the same fuel consumption. The dimensions of calcining furnaces show the following range: height 8 to 16

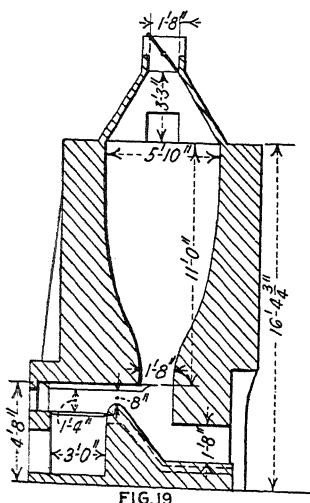


FIG. 19

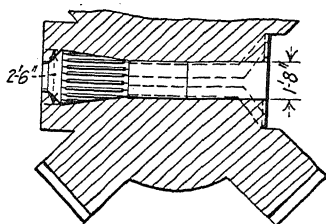


FIG. 20

FIGS. 19 and 20.—Calcining furnace with fireplace.

ft., width at throat 5 ft. to 5 ft. 9 in., at fireplace 1 ft. 8 in. to 2 ft. The illustration shows the heavy furnace walls which used to be common. A modern type of such a furnace with three fire places resembles the quicksilver furnace of New Almaden.²

In recent years the Spirek automatic furnace, first employed for roasting of cinnabar, has been used for calcining medium size oxide zinc ore. At Ponte di Nossa³ a furnace treats in 24 hr. 10 to 11 tons carbonate ore with a fuel consumption of 8 per cent on the raw ore, and is served in 8-hr. shifts by 3 men and 2 boys.

Fine ores are calcined in reverberatory furnaces. Hand reverberatories used to be the rule. A furnace with hearth 40 ft. long and 8 ft. wide, with roof 24 in. high at center, worked from one side through doors 6 ft. apart, and fired from a grate 18 by 48 in., will calcine in 24 hr. 8 tons of ore, require 10 per cent coal, and 2 men on an 8-hr. shift; 2 tons are drawn and charged every 6 hr. A furnace

¹ *F., Rev. Un. Min.*, 1862, XI, 254.

² Christy, *Tr. A. I. M. E.*, 1884-85, XIII, 561, Plate III.

³ *Min. Ind.*, 1901, X, 687.

with superposed hearths, each 16 ft. 6 in. long and 8 ft. wide, worked from one side, will do similar work.

The Ferrari furnace, in operation at Monteponi, Sardinia,¹ consists of a pair of inclined hearths, side by side, each 38 ft. 4 in. long by 6 ft. 6 in. wide, with a slope of 1 ft. in 3.5 ft., having working doors on the side. It is fired from a Boëtius gas producer with step-grate, the gases from both hearths pass off through a common stack. Ore is charged and drawn every 4 hr., remains in the furnace 25 to 30 hr.; each furnace treats in 24 hr. 20 to 21 tons ore, which loses 25 per cent in weight, and is served in 24 hr. by 5 men; the furnace is fired with lignite (4,800 Cal.), the fuel consumption is 9.8 to 10.0 per cent of the weight of the ore.

The Matthiessen and Hegeler zigzag furnace² used at one time at Lasalle, Ill., may be noted as a matter of record.

The Oxland-Hocking furnace, which is called in the United States White-Howell or White furnace, and used for drying, for oxidizing and for chloridizing roasts, is a revolving inclined boiler-iron cylinder lined with firebrick. It is fed continuously at the upper end and fired at the lower. Such a furnace in operation at Buggeru, Sardinia,³ is 42 ft. long, 2 ft. 10 in. in diameter, has a slope of 1 ft. in 18 ft., and a fireplace 3.5 ft. square. The brick lining, $4\frac{1}{2}$ in. thick, shows four longitudinal ribs projecting $4\frac{1}{2}$ in. The furnace makes 15 r.p.m., treats in 24 hr. 12 tons ore which passes through it in 4 hr., and loses 28 per cent in weight; the fuel required is from 8 to 14 per cent of the weight of calcined ore, the wide range covering the use of bituminous coal and lignite. A 30-ft. furnace fired with an 8-ft. Taylor gas producer was in operation in Virginia at the Bertha works.⁴

In a modern plant, mechanical roasting furnaces, common in treating sulphide copper ores⁵ would probably be selected to handle large quantities of ore.

50. Roasting Blende, General.—The object of roasting blende is to convert ZnS into ZnO and to expel the SO_2 formed. Desulphuri-

¹ Ferrari, *Oest. Zt. Berg. Hüttenw.* 1886, XXXIV, 655; *Proc. Engl. Instit. Civ. Eng.*, 1888, XCI, 559.

Marx, *Zt. B. H. S. W. i. P.*, 1892, XL, 275.

² Strecker, *Oest. Jahrb.*, 1879, XXVII, 316.

³ *Proc. Engl. Inst. Civ. Eng.*, 1888, XCI, 559.

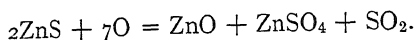
Marx, *Zt. B. H. S. W. I. P.*, 1892, XL, 275.

Ferraris, *Oest. Zt. Berg. Hüttenw.* 1892, XL, 233.

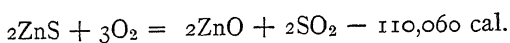
⁴ *Eng. Min. J.*, 1893, LVI, 544.

⁵ Hofman, "Copper," 1918, p. 9, 116.

zation of blende is not an easy matter, as many factors come into play which retard the process and make the result unsatisfactory; all roasted blende retains some S, from 0.5 to 4 and even 5 per cent, the S being present mainly as sulphide-S and to some extent as sulphate-S. The behavior of blende in roasting may be expressed by



The relative amounts of ZnO and ZnSO₄ formed are governed by temperature, free access of air, presence of other metallic sulphides and other factors. Heating ZnSO₄ (§27) to 702°C. converts it into 3ZnO · 2SO₃, and this basic salt gives off its SO₃ readily at 767°C. Therefore, with complete elimination of S the reaction taking place would be



The ignition temperature of Spanish blende with 0.30 per cent Fe is given by Friedrich¹ as 647°C. when 100-mesh, and 810°C. when 50-mesh. According to Hofman² blende from Joplin, Mo., with 0.45 per cent Fe, ignited at 480°C.; from Warren, N. H., with 8.80 per cent Fe, at 557°C., when through 8- and on 12-mesh, and at 515°C. when through 80-mesh; from New Mexico with 13.4 per cent Fe, at 534°C. The researches of Minor³ and Lepiarczyk⁴ corroborate the fact that ferruginous blende has a higher ignition temperature than one that runs low in Fe. In general, the ignition temperature can be said to lie between 550° and 600°C. On the other hand, when the roast has been started, a ferruginous blende roasts more quickly than one that is free from Fe.⁵ The data above show also that blende when fine kindles at a lower temperature than when coarse. Upon heating, some blende minerals decrepitate, others do not; the Spanish blende of Friedrich did this at 40°C., the Warren blende of Hofman did not, those of Joplin, Mo., and New Mexico decrepitated at 290°C. Blende from younger geological formations is said to roast more readily than from older.⁶ The behavior of blende upon heating is seen to vary as is the case with other sulphides, notably

¹ *Metallurgie*, 1909, VI, 179.

² *Tr. A. I. M. E.*, 1905, XXXV, 811.

³ *Chem. Z.*, 1889, XIII, 1602; *Berg. Hüttenm. Z.*, 1889, XLVIII, 466.

⁴ *Metallurgie*, 1909, VI, 409.

⁵ Nemco, *Metallurgie*, 1912, IX, 516.

⁶ Jensch, *Zt. angew. Chem.*, 1894, VII, 50; *Berg. Hüttenm. Z.*, 1894, LIII, 299.

e.g. with pyrite which shows ignition temperatures ranging from 260° to $500^{\circ}\text{C}.$ ¹ On the whole blende roasts slowly, the mineral does not swell and become porous; air for oxidation has to penetrate the surface of oxide² to reach the center of sulphide. Coarse blende can not be roasted satisfactorily, lump ore retaining 8 to 10 per cent S. With very fine blende, such as flotation concentrate, the particles lie too closely together to allow air to have the necessary free access; such material therefore has to be stirred, but doing this causes much dust to form; it also retains more S than coarser material. The usual size is about 8-mesh;³ some plants⁴ use a 5-mesh revolving screen with No. 14 wire, or a 6- or 7-mesh with No. 16 wire. A low temperature, limited access of air, weak draft, insufficiency of renewal of surface cause a slow roast and with this a condition favorable for some of the SO_2 set free to be converted by catalysis into SO_3 , which in part combines with ZnO to ZnSO_4 ; the decomposition of the ZnSO_4 into ZnO and SO_3 takes time even when the temperature is raised well above the one required for complete dissociation. It is necessary for a satisfactory roast to rabble the ignited blende frequently in contact with air and in addition to have toward the end a temperature of 800° to $850^{\circ}\text{C}.$ to decompose completely the ZnSO_4 that has been formed. In the reverberatory furnaces the temperature near the firebridge is held at about $1,100^{\circ}\text{C}.$;⁵ in muffle-furnaces the highest temperature reached lies around $900^{\circ}\text{C}.$, the lowest at $600^{\circ}\text{C}.$; a reverberatory furnace requires the excessive heat in order to counteract the cooling effect of the excess air which can not be excluded. Examples of temperature measurements in a Hegeler kiln are given in §64.

51. Influence of Impurities.—The result of a roast depends furthermore upon the associated sulphide and gangue minerals of the blende concentrate which may be favorable or not in the elimination of S. On the whole Met. S is likely to have a sulphatizing effect upon ZnO and thereby to retard desulphurization.

The most important sulphide minerals are those of Fe, Pb, Cu, As, Sb, Ag, Cb, and Hg; the gangue minerals, SiO_2 , CaCO_3 , MgCO_3 , FeCO_3 , CaF_2 , BaSO_4 , Sr_2SO_4 , and SnO_2 .

1. FeS and FeS_2 .—Pure FeS ignites in air at from 325° (100-mesh)

¹ Chalon, *Rev. Un. Min.*, 1902, LVII, 201.

² Orgler, *Zt. angew. Chem.*, 1890, III, 15; *Berg. Hüttenm. Z.*, 1890, XLIX, 128.

³ Ross, *Rev. Un. Min.*, 1894, XXIV, 38; *Berg. Hüttenm. Z.*, 1894, LIH, 314.

⁴ Johnson, *Met. Chem. Eng.*, 1917, XVI, 375.

⁵ Schnieder, *Oest. Jahrb.*, 1889, XXXVII, 393.

to 472°C. (>50-mesh); pyrrhotite Fe_8S_7 at from 430° to 590°C.¹ Oxidation may be expressed by $4\text{FeS} + 7\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$, and by $\text{FeS} + 2\text{O}_2 = \text{FeSO}_4$; $\text{FeSO}_4 + \text{Air} + 480^\circ\text{C.} = \text{Fe}_2\text{S}_2\text{O}_9 + \text{SO}_3$ and $\text{Fe}_2\text{S}_2\text{O}_9 + \text{air} + 560^\circ\text{C.} = \text{Fe}_2\text{O}_3 + 2\text{SO}_3$.¹ Heating FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ in a test-tube found, Friedrich² that at 700°C. both were decomposed into Fe_2O_3 , SO_2 , SO_3 ; this means that FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ in a blende charge is completely decomposed at 700°C. even surrounded more or less by SO_2 or SO_3 . According to Lepiarczyk,³ Fe_2O_3 acts upon ZnS with the formation of FeS and ZnO , and retards the elimination of S; on the other hand, Brandhorst⁴ gives the reaction $\text{Fe}_2\text{O}_3 + \text{ZnS} = \text{ZnO} + 2\text{FeO}$. Pyrite, which gives up 1 atom of S when heated to 700°C. with exclusion of air, ignites, as shown above, at temperatures ranging from 250° to 500°C.; it oxidizes more readily than pyrrhotite. The formation and behavior of zinc ferrite has been treated in §32.

2. *PbS*.—Galena⁵ ignites in air at 360° to 380°C. forming PbO , PbSO_4 , and SO_2 , the two solid products may react at about 700°C. with undecomposed PbS and form Pb and SO_2 . The PbSO_4 ⁶ is changed a 705° into $6\text{PbO} \cdot 5\text{SO}_3$ which sinters at 896°, fuses at 910°, and is decomposed into $2\text{PbO} \cdot \text{SO}_3$ at 952°C. when PbO is volatilized. The presence of galena is therefore sure to be harmful, as it is apt to sinter, envelop particles of zinc ore, and to increase the S-content of roasted ore. Decomposition of PbSO_4 by SiO_2 takes place at 1,040°C.⁷

3. *Cu₂S and CuS*.—As covellite loses 1 atom of S at a red heat, its behavior in roasting is about the same as chalcocite, except that being rendered porous, it ought to roast more quickly. Chalcocite⁸ ignites at temperatures ranging from 430° (100-mesh) to 697°C. (50-mesh), forming Cu_2O , CuO and CuSO_4 according to $\text{Cu}_2\text{S} + 3\text{O} = \text{Cu}_2\text{O} + \text{SO}_2$, $\text{Cu}_2\text{O} + \text{SO}_2 + \text{O}_2 = 2\text{CuO} + \text{SO}_3$, $\text{CuO} + \text{SO}_3 = \text{CuSO}_4$; but CuSO_4 ⁹ is converted at 670°C. into $2\text{CuO} \cdot \text{SO}_3$, and this at 736° into CuO and SO_3 . The sulphide,

¹ Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 534.

² Friedrich, *Metallurgie*, 1909, VI, 170.

Friedrich, *Metallurgie*, 1910, VII, 323.

³ *Metallurgie*, 1909, VI, 409.

⁴ *Oest. Zt. Berg. Hüttenw.*, 1905, LIII, 125.

⁵ Hofman, "Lead," 1918, p. 42.

⁶ Hofman-Wanjukow, *loc. cit.*

⁷ Friedrich, *Stahl u. Eisen*, 1911, XXXI, 2040.

⁸ Friedrich, *Metallurgie*, 1909, VI, 169.

⁹ Hofman-Wanjukow, *loc. cit.*

fusing at $1,127^{\circ}$ to $1,130^{\circ}\text{C.}$, will not interfere with the roast, and CuSO_4 being dissociated below 800°C. will not increase the S-content of the charge.

4. As_2S_3 .—Sulphide of arsenic is converted into As_2O_3 and SO_2 . The As_2O_3 is in part vaporized; in part it is converted into As_2O_5 , either in contact with an indifferent substance ($\text{As}_2\text{O}_3 + \text{SiO}_2 + \text{As}_2\text{O}_5 + \text{SiO}_2$), or in contact with a readily reducible oxide ($\text{As}_2\text{O}_3 + 2\text{Fe}_2\text{O}_3 \rightleftharpoons \text{As}_2\text{O}_5 + 4\text{FeO}$); the As_2O_5 may form metallic arsenate, stable at elevated temperatures.

5. Sb_2S_3 .—The oxidation of stibnite¹ may be expressed $\text{Sb}_2\text{S}_3 + \text{gO} = \text{Sb}_2\text{O}_3 + \text{SO}_2$, but Sb_2O_3 is further oxidized to Sb_2O_4 .

6. Ag_2S .—Argentite, melting at 808°C. , is converted by roasting into Ag_2 and SO_2 ; viz. $\text{Ag}_2\text{S} + \text{O}_2 = \text{Ag}_2 + \text{SO}_2$. The Ag may be converted into Ag_2SO_4 by SO_3 ; viz. $2\text{Ag} + 2\text{SO}_3 = \text{Ag}_2\text{SO}_4 + \text{SO}_2$; the SO_3 also has a sulphatizing effect upon Ag_2S ; viz. $\text{Ag}_2\text{S} + 4\text{SO}_3 = \text{Ag}_2\text{SO}_4 + 4\text{SO}_2$. The Ag_2SO_4 is dissociated in a current of air,² Ag_2SO_4 at $925^{\circ}\text{C.} = \text{Ag}_2 + \text{SO}_3 + \text{O}$, in a sulphurous atmosphere³ at $1,085^{\circ}\text{C.}$ The roasting of silver-bearing blende is likely to be accompanied by losses in silver. Sander⁴ investigated these losses with five ores which were treated in Maletra and Liebig-Eichhorn (§61) furnaces. He found that with a loss in weight of ore of from 10 to 12 per cent, the Ag-loss amounted to from 10 to 12 per cent with ore assaying from 67 to 120 oz. per ton. These figures appear to be high for the prevailing temperatures. Other data are furnished by Malaguti-Durocher,⁵ Plattner,⁶ and Simmonet⁷ who found high losses in their laboratory experiments.

7. CdS .—The roasted ore will contain some CdO ; a large part of the Cd will have been volatilized.⁸

8. HgS .—The oxidation of cinnabar is expressed by $\text{HgS} + 2\text{O} = \text{Hg} + \text{SO}_2$; Hg will be completely expelled.

9. SiO_2 .—This is unaltered in roasting. It may, however, combine with bases and form a sinter or a slag, both of which are detrimental to the expulsion of S.

¹ Hofman-Blatchford, *Tr. A. I. M. E.*, 1917, XLIV, 671.

² Hofman-Wanjukow, *loc. cit.*

³ Friedrich, *Metallurgie*, 1910, VII, 383.

⁴ *Zt. angew. Chem.*, 1902, XV, 335; *Min. Ind.*, 1902, XI, 611.

⁵ *Ann. Min.*, 1850, XVII, 17.

⁶ "Röstprocesse," 1856, p. 117.

⁷ *Ann. Min.*, 1870, XVII, 27.

⁸ Doeltz-Graumann, *Metallurgie*, 1906, III, 372.

10. CaCO_3 .—Calcite is decomposed by heat at 910°C .;¹ it is more or less attacked by SO_2 and SO_3 forming CaSO_3 and CaSO_4 . In the presence of air, CaSO_3 is changed into CaSO_4 ; in the absence of air, it is decomposed as follows: $4\text{CaSO}_3 = 3\text{CaSO}_4 + \text{CaS}$. According to Lepiarczyk² only 75 per cent of the CaO is converted into CaSO_4 in roasting, while Prost³ states that nearly all the CaO is present as CaSO_4 . Decomposition of CaSO_4 by heat takes place at $1,200^\circ\text{C}$.;⁴ by SiO_2 at $1,250^\circ$, the reaction beginning at $1,000^\circ$; by Fe_2O_3 also at $1,250^\circ$, the reaction beginning at $1,100^\circ$ and forming an eutectic, $\text{CaO} + \text{Fe}_2\text{O}_3$, which fuses at $1,250^\circ$ to a ruby-colored liquid. Hence, CaSO_4 once formed in roasting will be found unaltered in the roasted ore.

11. MgCO_3 .—This compound begins to lose CO_2 at 450°C .;⁵ magnesite in a closed tube is decomposed at 570°C .⁶ In roasting, MgCO_3 is converted into MgSO_4 , and this salt is readily changed into MgO and SO_3 at 972°C .⁷ Roasted blende is therefore likely to contain both MgSO_4 and MgO .

12. FeCO_3 .—Siderite is decomposed in a closed tube at temperatures ranging from 380 to 415°C .;⁸ the FeO will be readily peroxidized and show a behavior similar to that of Fe_2O_3 formed in the oxidation of Fe_xS_y .

13. CaF_2 .—Fluorspar is not common with blende; it is, however, a characteristic associated mineral in deposits of Illinois and especially of Kentucky, also of Northern Mexico. In roasting, the SO_3 and H_2SO_4 formed are found to set free HF , viz. $\text{H}_2\text{SO}_4 + \text{CaF}_2 = 2\text{HF} + \text{CaSO}_4$; the HF acts upon SiO_2 : $4\text{HF} + \text{SiO}_2 = \text{SiF}_4 + 2\text{H}_2\text{O}$; and $3\text{SiF}_4 + 3\text{H}_2\text{O} = 2\text{H}_2\text{SiF}_6 + \text{H}_2\text{SiO}_3$; further, H_2SiF_6 is decomposed by heating into SiF_4 and 2HF . These reactions are important if the SO_2 -gas is to be converted into H_2SO_4 , as the siliceous filling of the Glover tower and the lead of the acid chamber are attacked, and the acid becomes contaminated with SiO_2 .⁹

¹ Zavrieff, *Compt. rend.*, 1907, CXLIV, 428.

² Lindt, *Metallurgie*, 1909, VI, 409, 411.

³ *Bull. Soc. Chim. Belge*. 1911. XXV. 103; *Eng. Min. J.* 1911. XCII. 52; *J. Soc. Chem. Ind.* 1911. XXX. 366.

⁴ Hofman-Mostowitsch, *Tr. A. I. M. E.*, 1908, XXXIX, 628.

⁵ Brill, *Zi. phys. Chem.*, 1905, XLV, 283.

⁶ Friedrich, *Stahl u. Eisen*, 1911, XXXI, 1909; *Metallurgie*, 1912, IX, 409.

⁷ Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 565.

⁸ Friedrich-Smith, *Stahl u. Eisen*, 1911, XXXI, 1909; *Metallurgie*, 1912, IX, 409.

⁹ Prost-Lecocq, *Bull. Assoc. Belge. Chim.*, 1902, XVI, 99; *Min. Ind.*, 1902, XI, 610; *J. Soc. Chem. Ind.*, 1902, XXI, 861.

r) SO_4 .—Barite and celestite are found with blende, the former frequently than the latter. According to Mostowitsch¹ they are associated into BaO and SO_3 only at $1,500^\circ C$. and decomposed into SO_2 or Fe_2O_3 at $1,000^\circ C$. The behavior of $SrSO_4$ has not been subjected to a similar investigation. It is believed that both remain practically unchanged in roasting.

—Cassiterite is found only in a few occurrences of blende, being heavier than blende, the small amounts of the mineral are concentrated in a concentrate. The mineral is not attacked in the dry roast.

Free of Desulphurization.—The sulphur in roasted blende is S-side and S-ate sulphur. Prost's study² with two blends, one high in Pb and low in SiO_2 , contained Zn 49, Pb 10, CaO 0.5, MgO 0.4, SiO_2 1.2, S 19 per cent; the other low in Pb and high in SiO_2 , contained Zn 36, Pb 4, Fe 15, CaO 0.9, SiO_2 5, S 30 per cent, gave the results shown in Table 19. The results are given by Hassreidter-Trooz.³

**-SULPHIDE AND SULPHATE SULPHUR IN PERFECT AND IMPERFECT
ROASTS OF BLENDE**

Sulphur, per cent	Lead blende		Iron blende		
	Perfect roast	Imperfect roast	Perfect roast	Imperfect roast	
.....	2.10	5.33	2.91	7.73	
water-soluble.....	0.43	0.50	1.28	0.87	
water-soluble {	Zn.....	0.45	0.32	1.12	0.63
	CaO....	0.52	0.63	1.14	1.06
	MgO....	0.10	0.12	0.27	0.18
soluble in ammon.					
(PbSO ₄).....	1.34	0.31	0.72	0.36	
.....	0.33	4.52	0.91	6.50	

Following the progress of a roast it is necessary to test for S-ate sulphur. The presence of S-side, or *faulty*, sulphur is

ergie, 1909, VI, 450.

Min., 1900, XLIX, 247.

Chem., 1906, XIX, 522; *Eng. Min. J.*, 1907, LXXXIII, 707.

Chem., "Reduction des Minerais de Zinc par Electricité, p. 10, quoted in *Iron and Cadmium*" pp. 46 and 47.

"Zinc" pp. 226 and 233.

found by crushing a sample and then panning, the amount of concentrate found gives a close idea of S-ide present; or by melting in an iron spoon 2g. KClO_3 and sprinkling some of the sample into it, when the appearance of sparks will show that sulphide is present; or by warming a sample in a test-tube with dilute HCl in the presence of a strip of sheet zinc and a piece of paper soaked with lead acetate which becomes tarnished. The presence of S-ate sulphur can be tested by boiling with H_2O and adding BaCl_2 ; furnace men often place some of the sample on the tobacco of a pipe, when the presence of SO_3 will be tasted very quickly.

The extent to which desulphurization is carried varies, roasted ore free from compounds which fix sulphur, retain 1 per cent S and less; roasted limy and leady ores contain as much as 4 and 5 per cent total S. The progress of desulphurization in a 4-muffle Liebig-Eichhorn furnace (§61) treating three lots of clean Silesian blende in from 36 to 48 hr., given by Eilers,¹ is shown in Table 20.

TABLE 20.—DESULPHURIZATION OF BLENDE IN LIEBIG-EICHHORN FOUR-MUFFLE FURNACE

	I Per Cent S	II Per Cent S	III Per Cent S
Blende concentrate.....	19.2	26.8	26.5
End of muffle 1.....	17.6	19.10-21.90	15.4-21.3
End of muffle 2.....	12.0	11.20-14.30	9.9-12.4
End of muffle 3.....	3.4	1.02- 1.48	0.75- 1.06
End of muffle 4.....	0.6	0.35- 1.02	0.75- 1.00

The S-content of the roasted ore influences the yield of zinc in the retort. It is usually held that 1 unit of S holds back 2 units of Zn. Forcing a roast to reduce the S-content is likely to be accompanied by a considerable loss of zinc by volatilization, and prolonging the roast beyond a given time is too expensive, hence, it may be wiser to leave more S in the roast than would appear advisable in considering the total S. In fact, sulphate-S is likely to be harmless (§27) and often it is not considered at all.² Large-scale reduction tests by Prost³ with the leady and irony blende ores, noted above,

¹ *Tr. A. I. M. E.*, 1891, XX, 338.

² *Heid Eng. Min. J.* 1896, LXII, 178.

Mackay, *loc. cit.*, p. 291.

³ *Rev. Un. Min.*, 1900, XLIX, 247; *Berg. Hüttenm. Z.*, 1900, LIX, 624; *Oest. Zt. Berg. Hüttenm.*, 1900, XLVIII, 607.

showed that with well-roasted leady ore, the retort residue assayed 1.35 per cent Zn, and 7.38 per cent when imperfectly roasted; with iron ore well-roasted residue showed 0.95 per cent Zn, and imperfectly roasted 6.70 per cent Zn. This points to the desirability of carrying the roast as far as is permissible under given conditions. The results show also that leady ore gives a lower yield than iron; the higher extraction with the latter is explained, in part at least, by the decomposing effect reduced Fe has upon ZnS. Other data are furnished by Brandhorst.¹

The loss in weight of a blende ore in roasting is two-fold. The theoretical loss can be calculated from the changes the ore undergoes; ZnS loses 16.5 per cent in weight by conversion into ZnO; PbS and CaCO₃ diminish the loss, FeS₂ increases it. The roasting loss lies between 10 and 20 per cent. The actual loss in weight is greater on account of the dust loss. With ordinary concentrates it ranges from 1 to 3 per cent; with the arrival of flotation concentrates the figure has risen to 20 per cent. The loss of zinc by volatilization is low; it is higher with reverberatory than with muffle furnaces; it should not exceed 1 per cent, and is usually less, especially in muffle furnaces.

53. Roasting Furnaces, General.²—Roasted blende which is to be charged into a retort should contain as little S as practicable, hence, heaps, stalls and coarse-ore furnaces are out of place; automatic fine-ore kilns, such as the Gerstenhöfer furnace³ might be used if the operation were divided into roughing and finishing, but even in such a case other furnaces are preferable, so that the venerable Gerstenhöfer will hardly be considered. There remain reverberatory and muffle furnaces which furnish products low in S, the ore being raked either by hand or mechanically. Reverberatory furnaces furnish gases which are low in SO₂, about 1 per cent vol., and are contaminated with the gases from the heating fuels;

¹ *Zt. angew. Chem.*, 1904, XVII, 505; *Oest. Zt. Berg. Hüttenw.*, 1905, LIII, 125.

² Ingalls, *Min. Ind.*, 1903, XII, 366; *Eng. Min. J.*, 1912, XCII, 42; 1915, XCIX, 420.

Schütz, *Metallurgie*, 1911, VII, 653 (transl., Hahn, *Eng. Min. J.*, 1912, XCIII, 557); *Metall u. Erz*, 1915, XII, 109.

Nemes, *Metallurgie*, 1912, IX, 516.

Hommel, *op. cit.*, 1912, IX, 281 (transl., Hahn, *Eng. Min. J.*, 1912, XCIV, 697, 752).

De Lummen, *Eng. Min. J.*, 1916, CI, 1021; CII, 741.

Chase, *op. cit.*, 1917, CIV, 698.

³ Hofman, "Copper," 1918, p. 87.

they can not be utilized for the manufacture of H_2SO_4 or H_2SO_3 , and either pass off into the open direct, where this is permissible, or first have to be rendered harmless by neutralizing agents. Muffle furnaces, on the other hand, furnish gases free from the combustion gases of heating fuels and run high in SO_2 —4 per cent vol. and over—to permit their conversion into H_2SO_4 or H_2SO_3 . In the United States reverberatory prevail greatly over muffle furnaces,¹ while in Europe the reverse is the case; the difference in cost of labor has been the main cause of hand-rabbed reverberatories and muffles being uncommon in the United States and more general in Europe.

54. Reverberatory Furnaces Raked by Hand.—These furnaces have stationary hearths of much greater length (40 to 60 ft.) than width (8 to 14 ft.). A furnace 8 to 10 ft. wide is worked from one

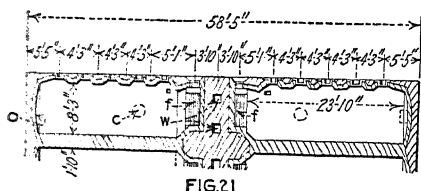


FIG. 21

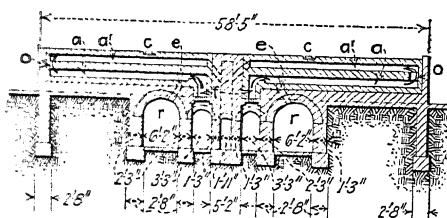


FIG. 22

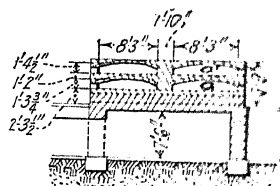


FIG. 23

FIGS. 21, 22 and 23.—Block of four 2-hearth hand-raked reverberatory furnaces, Hohenlohe Works, Silesia.

side, a furnace 14 ft. wide from both sides; narrow furnaces are common with blende, as the control is given to a single man responsible for the result. The fireplace is at one end and the flue at the other. The ore is charged at the flue-end and transferred in stages to the fire-end where it is discharged. The older furnaces had single hearths, later two superposed were common in order to obtain a better utilization of heat and a saving of floor space and of roof, but this saving is obtained at the expense of convenience of working.

¹ Eng. Min. J., 1915, XCIX, 421.

Three- and four-hearth furnaces have been in operation in Kansas, and 8-ft. furnaces at La Salle, Ill.¹

The general shape of a single-hearth reverberatory furnace is easily seen from Figs. 21 to 23, which represent a block of four double-hearth furnaces. A single-hearth furnace² with hearth 40 ft. long and 8 to 10 ft. wide, roof 16 to 18 in. high, grate 6.5 by 1.5 ft., four working doors on a side, will treat 3 tons blende in 24 hr. with a little over 1 ton coal and 2 men. Every 6 hr. there are charged 1,500 lb. raw ore, and every 4 hr. there is withdrawn an amount of roasted ore equivalent to 1,000 lb. raw ore; a charge is raked for $\frac{1}{4}$ -hr. at intervals of 4 hr. The draft of the furnace is strong, being furnished by a stack 3 ft. 2 in. square and 82 ft. high; the fluedust amounts to 1 per cent of the charge. The progress of desulphurization in such a furnace is shown in Table 21, the data refer to a certain blende of which the details are missing.

TABLE 21.—DESULPHURIZATION IN A SINGLE-HEARTH REVERBERATORY FURNACE, CORPHALIE, BELGIUM³

Sample, per cent	Zinc sulphide, per cent	Zinc sulphate, per cent	Zinc oxide, per cent
C	64.5	0.0	0.0
2	58.0	3.4	4.6
3	38.0	7.9	19.0
4	17.5	8.4	39.0
5	10.0	2.6	50.5
D	1.2	2.2	59.7

A block of four double-hearth reverberatory roasting furnaces of the Hohenlohe works, Silesia,⁴ is shown in Figs. 21 and 23. Four two-hearth furnaces, with hearths 23 ft. 10 in. by 8 ft. 3 in. and five working doors to a hearth, form a block; the four fireplaces are near the center in order to facilitate the handling of coal and ashes, and to permit the removal of gases by one main flue. At a time there are in the furnaces three charges of 2,200 lb., two on the upper and one on the lower hearth. A charge is drawn and dropped every 5 hr., the ore therefore remains 15 hr. in the furnace. The ore in a furnace is raked every half hour; the raking of the four

¹ Strecker, *Oest. Jahrb.*, 1879, XXVII, 316.

² Thum, *Berg. Hüttenm. Z.*, 1876, XXXV, 202.

³ *Min. Ind.*, 1893, II, 648.

⁴ *Oest. Jahrb.*, 1889, XXXVII, 389.

furnaces is so timed that the gases in the main flue may have approximately a uniform composition which is essential for their further treatment. The charge on a lower hearth is spread to half the thickness of that on the upper hearth in order to obtain a better desulphurization; the temperature at the firebridge is not allowed to exceed $1,100^{\circ}$ to $1,200^{\circ}\text{C.}$, as otherwise the loss of zinc by volatilization becomes excessive. The loss in weight ranges from 10 to 20 per cent depending upon the character of the concentrate (coarse, medium, fine). Two men in a 12-hr. shift attend one furnace including the firing; the fuel consumption is 35 per cent on raw ore. The gases from 14 furnaces (three blocks of 4 and one of 2 furnaces) contain SO_2 1, CO_2 3.5, O 16, N 79.5 per cent vol. They travel through dust chambers, pass up and then down in two condensation towers through which falls a fine spray of milk of lime. The daily consumption of lime is 6.5 tons. The lime collected in the settling basin contains CaO 40, CO_2 2.5, SO_2 37.5, SO_3 4.0, $\text{Fe(Al)}_2\text{O}_3$ 3.4, Insol. 8.0 per cent; it is dried, ground, and sold as fertilizer. The fluedust collected in the dust chamber, about 1.5 per cent on the raw ore, contains Zn 25, Pb 3, Fe 8.1, SO_3 50 per cent.

The progress in desulphurization in a similar furnace at Flône, Belgium, is given in Table 22.¹ The data refer to a certain furnace

TABLE 22.—DESULPHURIZATION IN TWO-HEARTH REVERBERATORY ROASTING FURNACE, FLÔNE, BELGIUM

Sample, per cent	Zinc sulphide, per cent	Zinc sulphate, per cent	Zinc oxide, per cent
C	83.0	0.0	0.0
2	70.5	3.7	15.2
3	52.2	3.9	34.6
4	51.5	4.2	38.0
5	43.0	11.0	41.5
6	23.2	12.3	57.8
7	17.7	7.8	65.0
8	8.6	6.2	75.5
D	1.9	5.9	81.0

in which a given ore is treated in a prescribed way; they have, however more general application in showing the decrease of ZnS, increase of ZnO, and formation of ZnSO_4 until a maximum is reached

¹ *Min. Ind.*, 1893, II, 648.

which is reduced later, but ZnSO_4 is not completely eliminated. Data relating to Oberhausen and Ämmeberg are given by Mahler.¹ The cost of roasting in a hand reverberatory furnace is about \$2 per ton of raw ore.

55. Reverberatory Furnaces, Raked Mechanically.—The largest item in the cost of roasting in a hand reverberatory furnace is that of manual labor which amounts to over 50 per cent of the total. The roasting man has to transfer the ore from feed to discharge and to rabble it frequently in order to expose new surfaces of sulphide to oxidation; rabbling once in 30 min. is a cause of the small tonnage of hand roasters. Mechanical rabbling, say once in 5 min., is more effective and likely to be cheaper than handwork; the same is the case with the transfer of the ore. On account of the high cost of labor in the United States mechanical has almost wholly replaced manual work; it does the work more cheaply in spite of the greater cost of furnace and repair, and the need of power. The greatest variety of mechanical furnaces is to be found in connection with rough roasting of sulphide copper ores.² Many of these furnaces have been used in dead-roasting blende, but only a few are in operation at present. Some of these are the furnaces of Brown, Ropp-Capreau, Zellweger, and Rissman-Ruebel which are discussed below. The older furnaces are those of Ross-Welter,³ Pearce, Edwards, Merton,⁴ Godfrey,⁵ Blake,⁶ Brückner,⁷ Howell-White, etc.

56. Brown Horseshoe Furnace.—There exist three forms of Brown reverberatory furnaces, the horseshoe used for sulphides in general, the elliptical⁸ in operation at one time for roasting gold-silver ores to be chlorinated, and the straight-line⁹ intended for general work.

The Horseshoe Furnace¹⁰ is the only form that has been and is being used for blende; of the 99 mechanical reverberatory roasters in operation in 1915 in the United States, 14 were of the Brown type. Figures 24 to 26 give a plan and two sections.¹¹ Figure 24

¹ *Ann. Min.*, 1885, VII, 514.

² Hofman, "Copper," 1918, pp. 116 and foll.

³ Mahler, *Ann. Min.*, 1885, VII, 519.

⁴ Hofman, "Copper," *loc. cit.*

⁵ Hofman, "Lead," 1918, p. 165.

⁶ *Tr. A. I. M. E.*, 1892-93, XXI, 943.

⁷ Hofman, "Copper," *loc. cit.*

⁸ Brown, *Eng. Min. J.*, 1896, LXII, 80.

Rothwell, *Min. Ind.*, 1896, V, 270.

⁹ Hofman, *Min. Ind.*, 1897, VI, 459.

¹⁰ Built by the Allis-Chalmers Co., Milwaukee, Wis.

¹¹ For five supplementary drawings, see Hofman, "Copper," 1918, p. 130.

shows a circular roasting hearth, *m*, 8 ft. wide, which occupies five-sixth of the annular space, while the remaining one-sixth forms an open space for the feed and discharge of ore, and for the cooling of rabbles. The hearth, 135 by 8 ft. = 1,080 sq. ft., is heated from three external fireplaces with grates 3 by 5 ft., thus giving a ratio of hearth to grate of 24:1. The first firebox is about 60 ft. from the feed-end of the furnace, the other two are 30 and 40 ft. apart. The flame enters the furnace through the roof, Fig. 26, and spreads uniformly under it; the stack, *i*, carries off the gases. In the center of the furnace is a slide-valve engine of 5 to 8 hp. which drives the mechanical feeder, *b*, and the endless cable, *c*, running over sheaves, *d*. On the inside opposite each sheave is a door, *e*, for oiling and repairing; on the outside opposite each second sheave is a door, *f*, to furnish access to the hearth. Figures 25 and 26 show on either side of the hearth a recessed chamber for the mechanism of the rabble-carriage which travels with double-flanged wheels on the inside rail and flat-tread on the outside rail; a continuous slot between the tiles *s* and *h* serves for the passage of the rabble-arms. There are in use two rabble-carriages *m*, with plow-shaped teeth, the carriages are attached alternately by automatic clamps to the traveling wire-rope, *c*; while one rabble-carriage, *m*, Fig. 24, is cooling in the open space, *l*, the other in passing through the furnace turns over and moves forward the ore. When it arrives in the open space, it pushes onward the cooled carriage, which is automatically clamped to the rope, *c*, and taking its place is detached from the rope. The change takes place every 2 to 3 min., the time it takes the rabble to pass through the furnace. The rabble-shoes are matched on the two arms so as to cover the whole surface; they can be lowered when they wear off or when it is desired to plow up crusts forming on the working bottom. The ore fed at *b*, Fig. 24, to a depth of 3 to 4 in. enters the hearth through swinging door, *j*, and is delivered after from 12 to 14 hr. at the other end through a similar door, *k*, into an ore-car. The furnace treats in 24 hr. 12 tons of blendé concentrate (S 24, Zn 56, Pb 1.5 per cent) reducing the S-content to 0.8 per cent, requires 8 tons refuse slack coal or 500,000 cu. ft. natural gas, 3 men on an 8-hr. shift, and makes 1 to 2 per cent fluedust. The cost of the furnace in 1913 was \$10,000; the cost of roasting \$1.50 to \$2 a ton. The advantage of Brown furnaces lies in the fact that the mechanical parts are protected from heat and gases, the disadvantage that the carriage is pulled from the inner side only and is likely to jump the track; it also limits the width of the hearth.

At the works of the Edgar Zinc Co., Cherryvale, Kan., there is in operation a modified horseshoe furnace, 130 ft. 10 in. outer diameter with a hearth 7 ft. 8 in. wide. The circle has two roasting hearths 140 ft. long, separated from one another by cooling spaces 30 ft. long. Each hearth has 8 gas inlets, its ore-feed and -discharge. The pair of hearths has four rabbles attached to a single cable which is driven from one 10-hp. motor. The rabbles travel over the entire circle; a rabble enters one furnace, travels through it in 30 sec., leaves it and remains in the open 60 sec., enters the second hearth, passes through in 30 sec., and cools in the second open space 60 sec. The hearths are gas-fired and burn 250,000 cu. ft. natural gas in 24 hr.; tests with fuel dust have been satisfactory. The two hearths roast in 24 hr. 25 tons blende concentrate, reducing the S-content to 1.00 per cent.

At the same plant there is in operation a straight-line Brown furnace with a pair of hearths, each 162 ft. long and 7 ft. wide, which differs from the one given in the reference on page 79. Each hearth has its fireplaces, ore-feed and -discharge, and rabble-frame with two sets of rabble-teeth; a single endless cable connected with a 20-hp. motor moves the rabble-frames of the pair of hearths. The rabble-frame of a hearth is pulled by the endless wire rope in 30 sec. over the hearth. During its passage it turns over and pushes forward the ore. On leaving the hearth it cools in the open for 30 sec., and then starts on its return trip over the hearth. The rabble-teeth are hinged so that during the return of the rabble-frame the teeth glide over the ore and stir, but do not move it. While the frame of one hearth travels in one direction, that of the other does just the reverse. When the frames have left the furnaces and traveled 30 ft. in the open, the motor is automatically stopped and its motion reversed. The motor is of 2-hp. A hearth roasts 10 tons blende concentrate in 24 hr., reducing the S-content of Joplin blende to 0.75 to 1.25 per cent.

57. Ropp and Cappeau Furnaces. *The Ropp Furnace.*¹—The Ropp furnace, shown in Figs. 27 to 30, is a straight-line reverberatory with hearth *a*, usually 150 by 14 ft., with four external fireplaces *b*, 5 by 4 ft., and a smoke flue *w*, 4 ft. 6 in. square. The hearth area, deducting the longitudinal slot, is 250 sq. ft.; the grate area 80 sq. ft., which makes the ratio of hearth to grate area 25:1; the smoke flue has an area of 10.25 sq. ft. Rakes *f* with blades *g*, drawn by an endless cable *p*, travel over the hearth and move the ore from the

¹ Built by Harron, Rickard & McCone, San Francisco, Cal.

feed *i* at one end to the discharge *j* at the other. Along the center of the hearth *a* runs a channel *c*, 1.5 in. wide, through which extend heavy trapezoidal steel-plate arms *d*, attached to four-wheel trucks *e*, each carrying a rake *f* of the width of the hearth with 32 teeth *g* set at an angle of 45 deg. Underneath the hearth is a longitudinal tunnel *o* in which are tracks *n*, 3 ft. 6 in. above the floor for the four-wheel trucks *e*. A furnace has six rakes working in pairs; four only are shown in Fig. 28. In a rake the 16 teeth covering one-half of the width of the hearth point outward, the 16 covering the other half inward, the rake is thus kept balanced. The 32 teeth of one rake are placed in directions opposite to those of the next following. If the ore is pushed outward and forward by one rake, it will be pushed inward and forward by the other, and will travel in a zigzag line over the hearth. The rakes enter the hearth at *h*, where the ore is introduced by a Challenge or other kind of mechanical feeder to a depth of 3 in., is stirred every 53 sec., and carried in 6 to 8 hr. to the discharge; in- and outlets are closed by swing doors *j*. The endless steel rope, $\frac{5}{8}$ in. in diameter, passes around horizontal sheaves *q* at the end of the furnace which make 1.63 r.p.m.; a horizontal shaft, making 75 r.p.m., transmits 6 hp. to one sheave through bevel and spur gears. Carriages with rakes make the return trip outside of the furnace and are cooled; the rope upon entering the furnace is sufficiently cool to allow touching with the hand, it lasts about 1.5 years. The furnace has doors on the side for the admission of air, for observation, and repairs. In furnaces heated with natural gas the fireplaces are omitted and the burners inserted in the sides as shown in the Cappeau furnace (Figs. 31 to 41). On account of the great length, the furnace is built in two sections to allow for expansion and contraction; the sections are joined by bars of channel iron which overlap and glide one within the other, they are tied independently so that the length of a tie-rod does not exceed 50 ft. The furnace treats in 24 hr. 20 tons blende (Zn 60, S 30, Fe 2, Pb 1) reducing the S-content to 0.8 per cent, requires 4 tons coal or 250,000 cu. ft. natural gas, one man per shift, and makes about 1 per cent flue dust.

A very satisfactory combination of a Ropp furnace and a Dwight-Lloyd sintering machine¹ has been made at Port Pirie, S. Austr.² The Ropp furnace usually roasts 15 tons blende in 24 hr., reducing

¹ Hofman, "Lead," 1918, p. 190 and foll.

² Rigg, *Min. Mag.*, 1918, XVIII, 285.

Riddell, *Eng. Min. J.* 1918, CVI, 119.

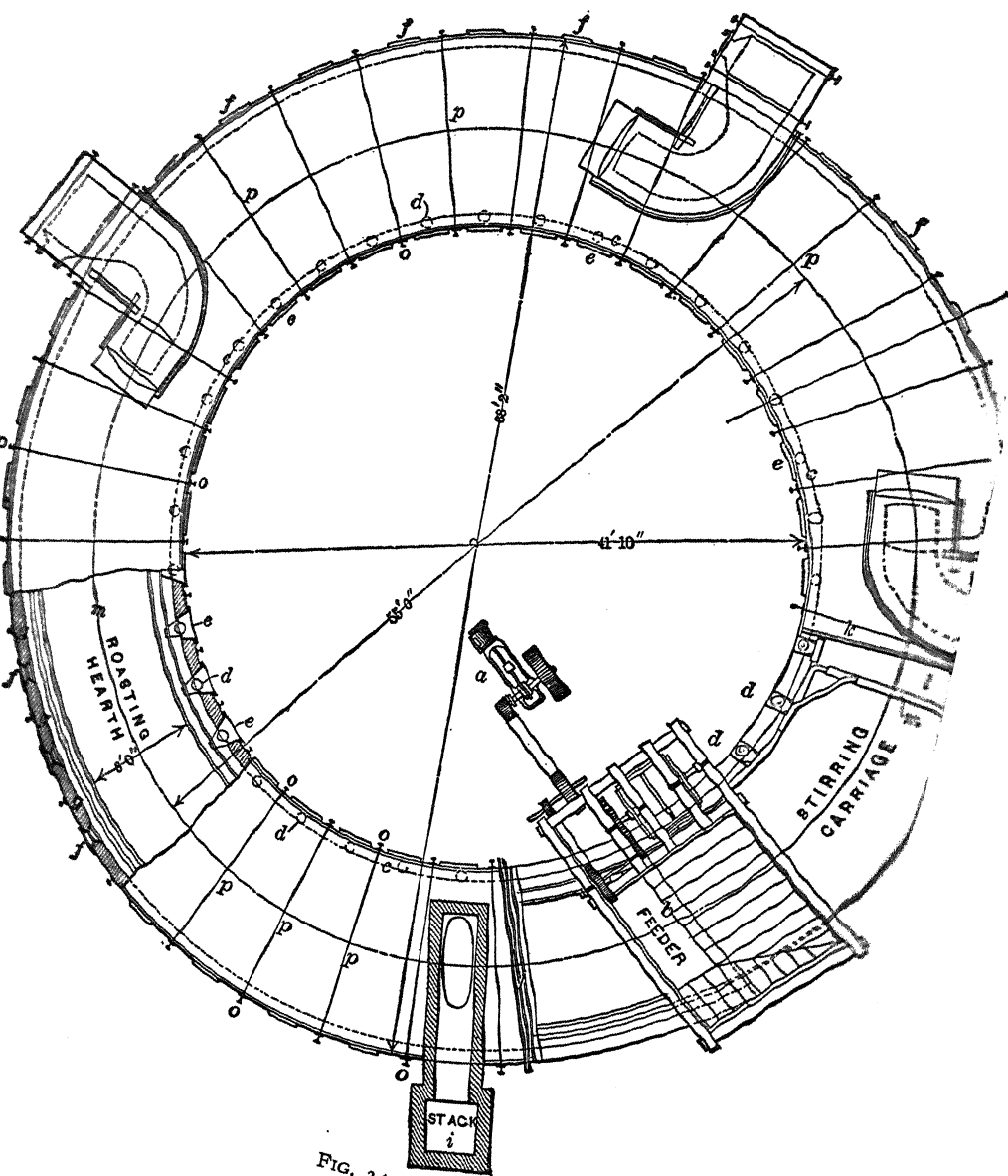
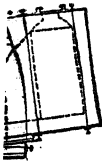
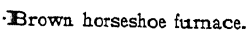


FIG. 24.

FIGS. 24, 25 and 26



SECTION OF FURNACE ON A.B.



(Facing page 82)

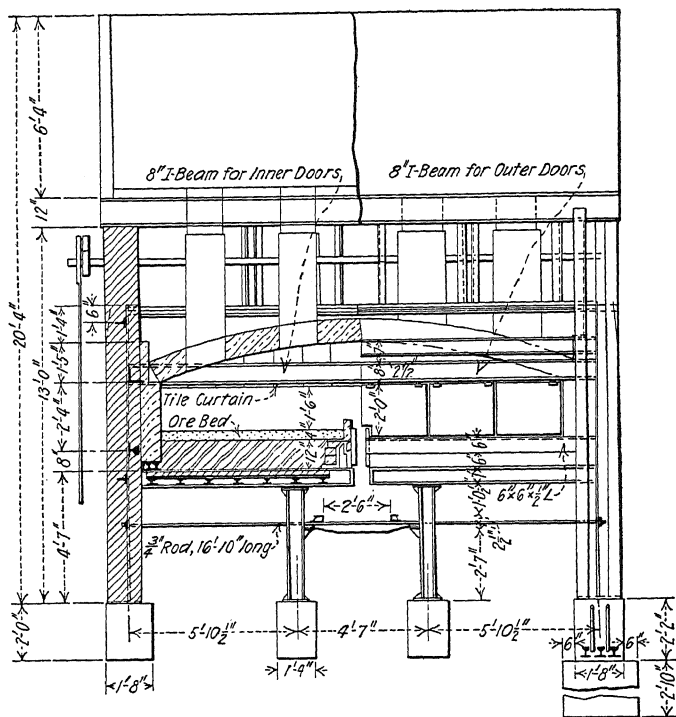
the S-content to 2 per cent; it rough-roasts 30 to 33 tons reducing the S-content to 10 per cent and consuming half the normal amount of coal. The rough-roasted ore is made up of kernels of sulphide with coatings of oxide. Working it on a D-L machine showed poor ignition and formation of about 10 per cent flue dust. Ignition troubles were corrected by the addition of raw blende; the reduction of dust from 10 to 2 per cent was effected by mixing in slime concentrate and water or in the absence of slime, 2 per cent plastic clay. A standard D-L machine treats in 24 hr. 90 tons pre-roasted ore with Zn 47 to 48 per cent and S 8 to 10 per cent, reduces the S-content to 1.5 per cent; it furnishes a crumbling sinter and a gas with 3 per cent SO_2 . In smelting the sinter, the retorts are charged with 16.6 per cent more ore, require 10 per cent less reducing fuel, and yield 4.3 per cent more spelter than with ore deadroasted in the Ropp furnace. It is the intention to replace the Ropp by an Herreshoff furnace and to send the D-L gas through the Herreshoff furnace, and thus recover 75 to 80 per cent of the S of the blende as H_2SO_4 . The coarse crumbling D-L sinter behaves in the retort as does oxide ore which is usually charged in sizes reaching $\frac{1}{2}$ in. The cost so far has been \$2.20 per ton of raw concentrate. Treating raw concentrate direct in the D-L machine caused clinkering on account of the excessive heat generated; mixtures of raw and roasted concentrate could be worked, but did not behave as well as did rough-roasted ore alone.

A Zellweger changed to a Ropp furnace which differs in some features from the standard is shown in Figs. 51 and 52.

The Cappeau Furnace.—The leading features of this furnace¹ are identical with those of the Ropp furnace. The chief differences are, that the roasting hearth is supported by an iron framework thus leaving the lower side of the hearth exposed to the air, and that the longitudinal slot is closed by tripping doors which are raised by the plates carrying the rabble-arms as they travel through the furnace, and drop again into their places after the passages of the arms; in this way the air entering through the slot is in part under control. The Cappeau furnace shown in Figs. 31 to 41, is gas-fired and supplements the discussion of the coal-fired Ropp furnace shown in Figs. 27 to 30. It was erected in 1912 at Collinsville, Okla., and is 150 ft. long and 15 ft. wide. Figure 31 gives longitudinal sections and side views; Figs. 32 and 33 a half end-view of the discharge end and half sections through the flue-end; Figs. 34

¹ U. S. Patent No. 691,112, Jan. 14, 1902.

port; the latter forms the working bottom which carries the ore to a thickness of 4 in. The longitudinal slot, Figs. 33 and 34, is enclosed by special castings protected from heat and roasting ore by brick



FIGS. 34 AND 35.

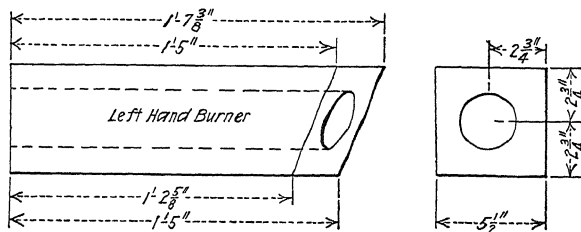


FIG. 36.

work, Fig. 34; at the opposite end are longitudinal rails, Fig. 33, which carry the side walls. At the charge end of the furnace is the receiving bin into which a traveling belt delivers the ore; at the

bottom of the ore bin are discharge openings (not shown) leading onto feed rollers which deliver ore continuously into the furnace through four chutes. Near the charge end is the flue opening, Figs. 31 and 33, 10 ft. by 11 in., which ends in a duct 30 by 33 in. terminating in a dust chamber, 12 ft. 6 in. by 8 ft. and 12 ft. 9 in. high, which has an arched roof sprung on a radius of 8 ft. 9 in.;

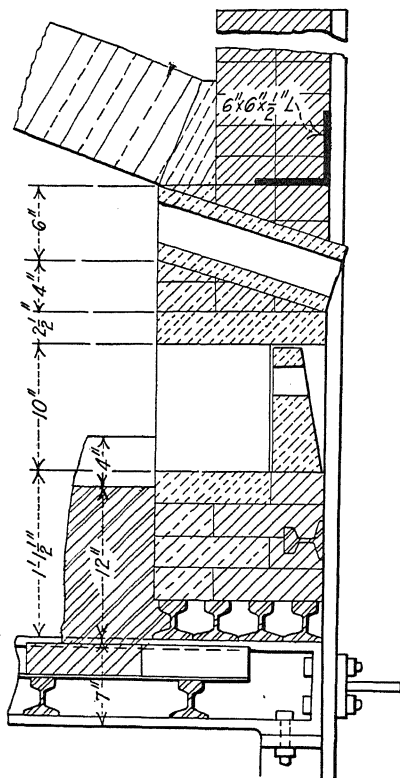


FIG. 37.

it delivers to a stack, 7 ft. in diameter (not shown). The feed end of the furnace is closed by inner and outer swing-doors, Figs. 31, 34, 35, the inner are placed at one end of the two bricked sections, Fig. 31, the outer at the other.

The furnace is fired with natural gas which enters through fire-tile burners. Figure 36 shows a left-hand burner. The locations of the burners are shown in Fig. 31 and the detail in Fig. 37. There are two burners to a section excepting the one near the discharge

end which has six. A burner, Fig. 36, is seen to be pointed upward, Fig. 37, in order that the flame may spread along the roof and heat the ore by radiation only. Beneath the burner is a tile which forms the roof of a window closed by a window-brick, Fig. 38. This serves to admit the necessary air and to permit access to the hearth; a tile, 18 by $13\frac{1}{2}$ by $2\frac{1}{2}$ in., serves to close the window when this is desired. The furnace has six rabbles which make the circuit in about 5 min. and stir the ore every 53 sec.

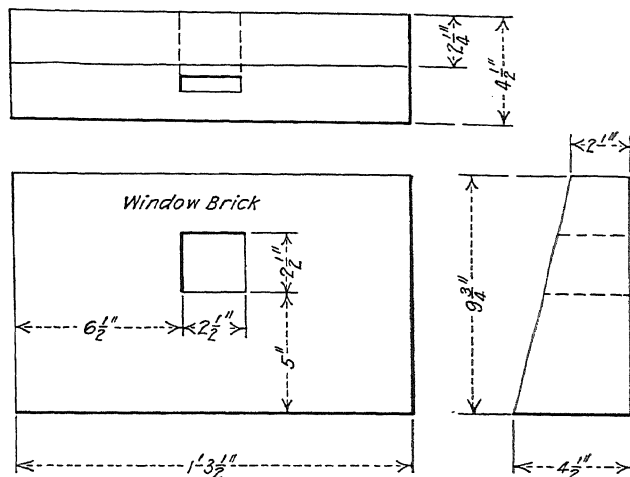


FIG. 38.

A rabble and carriage are shown in Figs. 39, 40 and 41. The rabble is a triangular frame made up of channel beams, *B*, back braces *C*, connected with *B* by channels *E*. To beam *B*, is attached adjusting plate *D* with vertical plow holders *H* and plow blades *I* (6 by 20 in. and $\frac{1}{2}$ in. thick). The steel rabble plate *A*, 46 by 46 in. and $1\frac{1}{4}$ in. thick, bolted to the frame is attached to the carriage; the latter has four guides *N* on a side to keep the wheels in position on the rails which are of 30-in. gage. To the middle of the carriage is attached a steel plate, $\frac{5}{8}$ by 4 in., which projects 20 in. beyond the plate and serves as a finger to raise the swing-doors closing the ends of the furnace. The steel rope forms sections between the carriages. In Fig. 41 one rope, on the back side of plate *A*, passes through an opening to the front side and is attached to a ratchet wheel, *T*, by means of which it can be tightened; the other rope, also on back side of plate *A*, passes through an opening to the front side and is there

clamped to the plate. In some furnaces the rabble carriage travels on the ground floor. While this simplifies the construction, it has the drawback of requiring a rabble plate of considerable height.

The work of the furnace is the same as that of the Ropp.

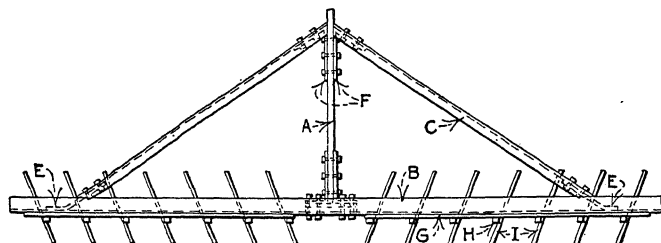


FIG. 39.—Plan.

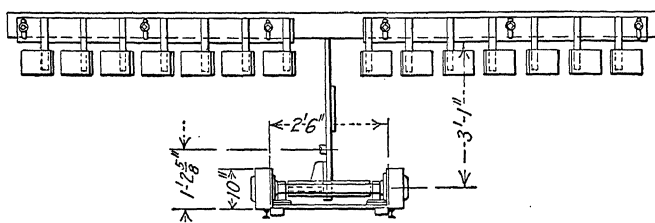


FIG. 40.—Front elevation.

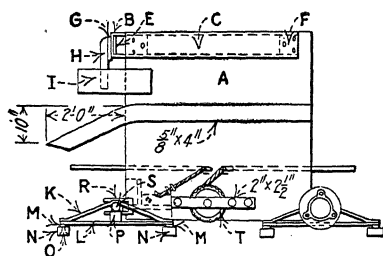


FIG. 41.—Side elevation.

One difficulty encountered with both furnaces is the paucity of air sucked in which retards oxidation and thereby reduces tonnage. This defect has been overcome by E. E. Godshalk at the Blackwell Works of the Bartlesville Zinc Co. by furnishing a furnace additional air under pressure and by withdrawing the sulphurous gases through two flues instead of one. A plan and part of a horizontal section of three Cappeau-Godshalk furnaces situated on one side of the main

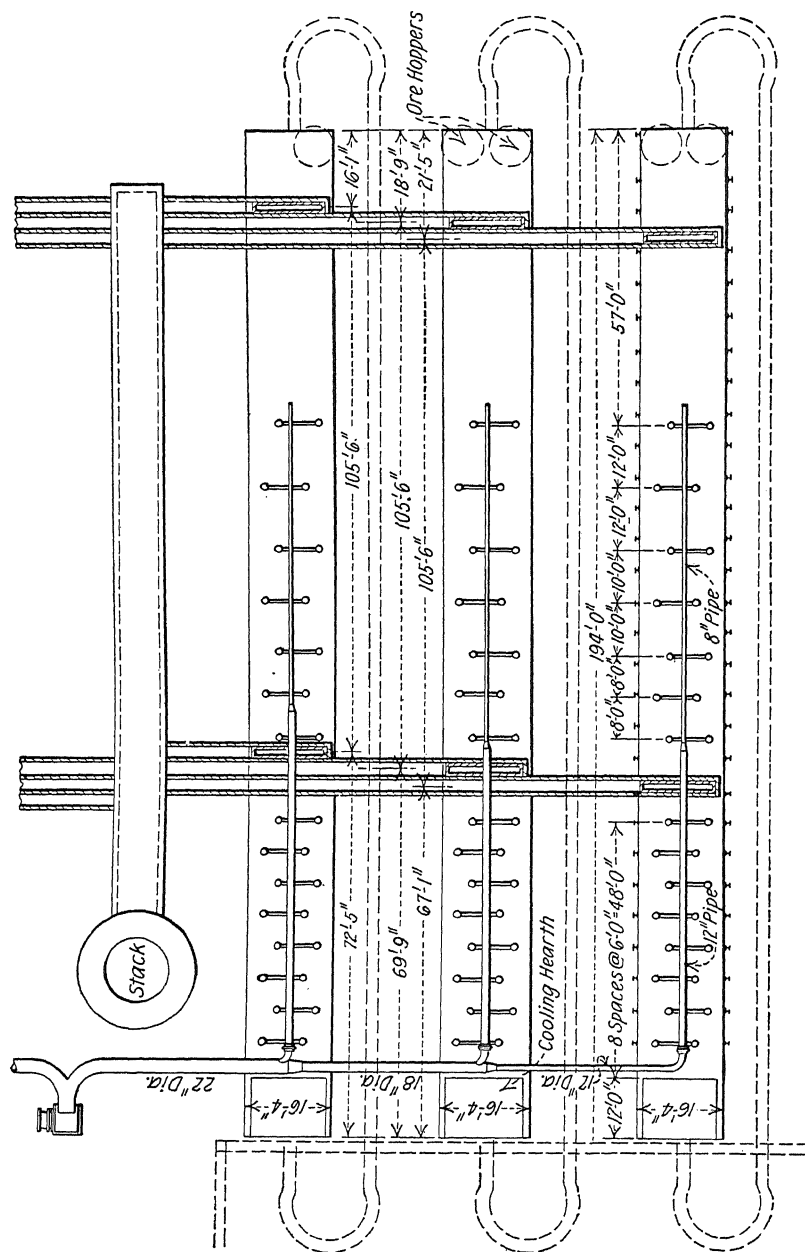
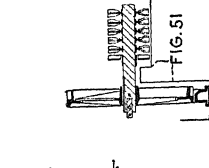
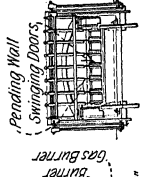
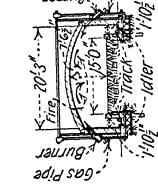
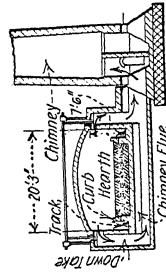
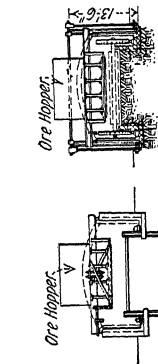
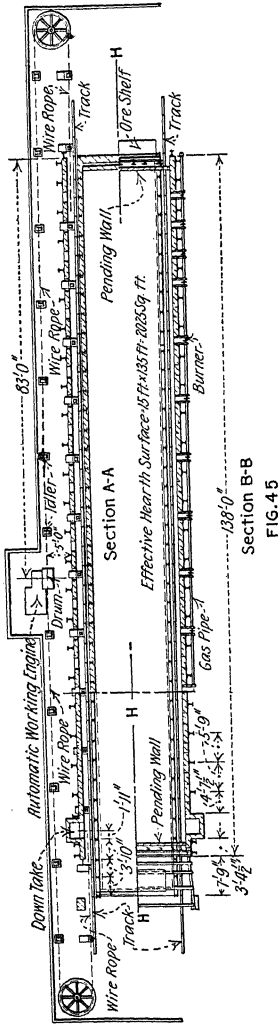
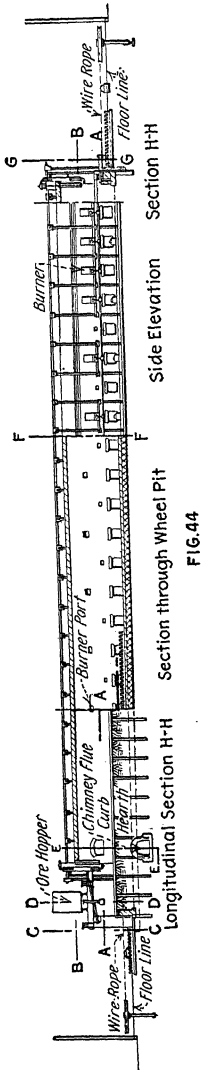


FIG. 42.—Cappeau-Godshalk furnace.

26 to 36 per cent S, remains in the furnace from 12 to 18 hr. depending upon its character and the depth of the bed; its temperature at the feed-end is $250^{\circ}\text{C}.$, at the middle from 700° to $750^{\circ}\text{C}.$, and at the discharge from 800° to $830^{\circ}\text{C}.$ The roasted ore retains from 0.5 to 1.5 per cent S according to the amounts of lime and lead present. The furnace treats in 24 hr. from 60,000 to 80,000 lb. blende, consumes from 250,000 to 350,000 cu. ft. natural gas, and makes from 1.5 to 2.5 per cent flue dust; one man fires three furnaces, one man trams the roasted ore from two furnaces.

A Ropp or Cappeau furnace cost in 1913 \$8,000 to \$10,000; the cost of roasting a ton of raw ore was about \$1.30; this was made up of 46 per cent for gas, 26 per cent for labor, 14 per cent for power, and 14 per cent for repairs and general expense.

58. The Zellweger furnace, Figs. 44 to 52, constructed in 1904, is another straight-line mechanical reverberatory roasting furnace which has found much favor in the United States. The characteristic feature of this gas-fired furnace (shown in part by side elevation and section in Fig. 44, by horizontal section in Fig. 45, by end elevations and cross-sections in Figs. 46 to 50, and by a detail of rabble in Figs. 51 to 52) is the method of rabbling the ore. The roasting hearth is 15 by 135 ft., representing an area of 2,025 sq. ft.; the roasting chamber, however, on account of the well-pits on the sides is 20 ft. 3 in. wide and has along the center line a height of 7 ft. $4\frac{1}{2}$ in., Fig. 49. The furnace is closed at the ends by pendent brick walls beneath which are suspended swinging doors, Fig. 50. At the feed-end is a rectangular ore-hopper, Figs. 46 and 47, with four feed pipes from the bottoms of which the necessary ore is drawn automatically by means of a movable distributing apron actuated by the passing stirrer wheels. At the discharge-end the roasted ore is pushed by the rabbles off the hearth on to an ore-shelf delivering into a car. The positions of the gas pipe and nine burners on either side of the furnace are shown in Fig. 47 and their locations in the side wall in Fig. 44; the downtakes and chimney are seen in Fig. 46. On either side of the hearth is a wheel-pit, Fig. 48, in which is placed a heavy air-cooled cogged track extending through the roasting chamber and a short distance beyond its ends, Fig. 44. The warmed air enters the roasting hearth. The tracks carry two cog wheels, 6 in. in diameter, joined by a shaft 7 in. in diameter, Fig. 49, on which are mounted the rabble-blades. The raking mechanism is operated by an endless wire rope, a drum and a 15-hp. engine controlled by an hydraulic device which automatically



FIGS. 44-52.—Zellweger furnace.

starts, stops, and reverses the movement. The wire rope is carried by two shafts at the ends and by idlers in the pit and outside the furnace. The shaft, Figs. 50 and 52, carries a number of collars each with eight steel trough-shaped blades. The collars, with blades forming a cylinder 2 ft. in diameter, extend over the width of the roasting hearth. They are free to revolve around the shaft when the latter travels toward the feed-end of the furnace; the convex side of the blades will drag through the ore, but will cause very little displacement. When the shaft travels toward the discharge-end, the collars are automatically locked on it by a ratchet device; the blades dig obliquely into the ore, scrape along the floor, the convex sides become filled with ore from the bottom, drag it forward and upward and spread it over the charge where it is exposed to heat and air. The stirrer makes one round trip and two stops in 8 to 10 min. Starting from the outside of the discharge-end, it opens the swing-doors, rolls through the roasting chamber and passes through the opposite swing-doors in 1.5 min., operates the feeding device, and stops 2 or 3 min. at the feed-end; on its return it passes over the hearth again in 1.5 min., and stops beyond the discharge-end where it cools for 3 or 4 min. The furnace treats in 24 hr. 25 to 30 tons Missouri blende concentrate with about 30 per cent S, furnishes 24 tons roasted product with 0.3 per cent S, the S present as CaSO_4 having been deducted; requires about 600,000 cu. ft. gas; makes little flue dust on account of the high arch of the roof which reduces the speed of the gas currents; demands 12 to 15 hp. and one man; the cost of repairs is low, a cable lasting 3 months.

While the work of the furnace is very satisfactory, its great disadvantage is that it consumes large amounts of natural gas,¹ owing mainly to the great height of roof.

The excessive gas consumption has been the reason for changing a Zellweger furnace roasting 25 tons blende concentrate in 24 hr. into a Ropp furnace of the same tonnage at the works of the Lanyon-Star Smelting Co. at Bartlesville, Okla., which resulted in a reduction of the gas consumption of 600,000 to 700,000 cu. ft. in 24 hr. to one of 250,000 to 300,000 cu. ft. The leading features of the Zellweger-Ropp furnace are given in Figs. 53 and 54.

The horizontal section, Fig. 53, shows the hearth to be 158 ft. 1 in. long and approximately 18 ft. wide; the rope-drive is similar to that of the standard furnace excepting that the engine is reversing

¹ Ingalls, *Min. Ind.*, 1907, XVI, 929.

because the pair of rabble-arms on a single car makes its return trip through the furnace instead of outside. For this purpose there are placed in the main tunnel, Fig. 54, outer and inner rails, the former being $3\frac{1}{2}$ in. lower than the latter. As the car travels on the outer rail from the green-ore end, Fig. 53, to the cooling hearth,

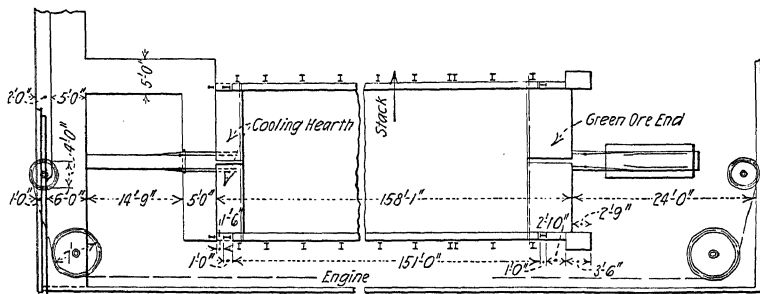


FIG. 53.

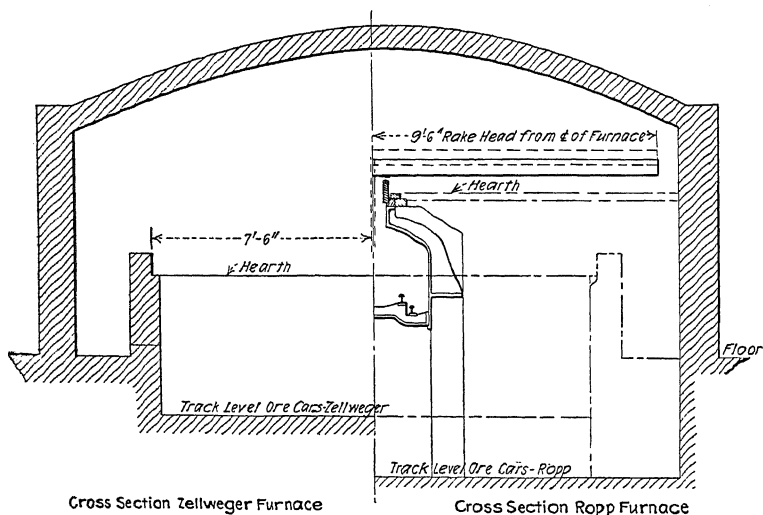


FIG. 54.

FIGS. 53 and 54.—Zellweger-Ropp furnace.

the rabble-blades turn over and push forward the ore. Leaving the hearth, the car comes to a stop and remains stationary for a few minutes; starting on its return trip, it is switched on to the inner rail and travels over the hearth without touching the ore. At the green-ore end it leaves the furnace, cools in the open for a few minutes and is switched on to the outer rail.

The half cross-sections of the Zellweger and the Zellweger-Ropp furnaces show the changes that have been made. The height of the arch has been reduced from 7 ft. 6 in. to 4 ft. 9 in., and the width increased approximately from 15 ft. to 18 ft. The cross-section of the Zellweger furnace of 136.6 sq. ft. has been reduced to the 72.0 sq. ft. of the Ropp. This gives the ratio of width to area of cross-section as 1:9.1 with the Zellweger, and as 1:4 with the Ropp.

59. Rissman-Ruebel Furnace.¹—This furnace, in operation at the works of the National Zinc Co., Bartlesville, Okla., is shown in cross-section in Fig. 55. Two parallel straight-line furnaces with hearths 150 by 8 ft. are fired with natural gas from burners placed in the roofs. The roof of a furnace is carried on the outside by the furnace wall and on the inside by hangers attached to I-beams. The ore, fed at the ends of a pair of furnaces, is stirred and moved to

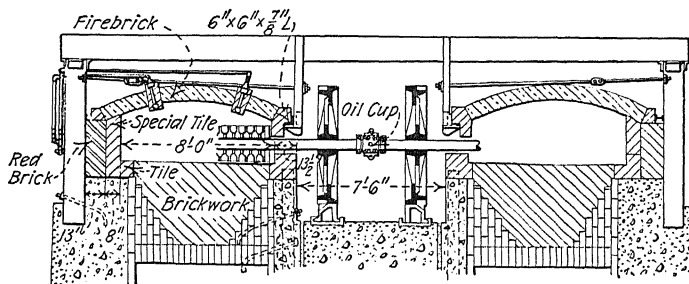


FIG. 55.—Rissman-Ruebel furnace.

the discharge by Zellweger rabblers attached to a single shaft which revolves in bearings on a carriage running on a smooth track. The carriage (not shown) consists of a framework of I-beams; the rabble-shaft is revolved by being geared to the axle of the carriage. The two continuous slots on the inner side of a pair of furnaces are closed by tripping doors which are raised by the shaft and drop again into place. The furnace has the advantage over the Zellweger in that the reduced widths of the hearth, permit a diminution of the height of the roof and thereby a saving in the quantity of gas required to maintain the necessary temperature; on the other hand, the continuous opening of the tripping doors either allows too much cold air to enter the furnace or fumes to escape into the building; in addition the general experience with these tripping doors in rough-roasting sulphide-copper ores in Montana² has been

¹ Editor, *Eng. Min. J.*, 1915, xcix, 326.

² Wethey and Keller furnaces, Hofman, "Copper," 1918, pp. 123, 126, 128.

that in a short time new doors ceased to close the openings satisfactorily. After the rabbling apparatus had been put into operation, it was found that the carriage and tripping doors did not function as was expected. The carriage has been replaced by the Zellweger stirrer wheels and line of racks, and a continuous slot is left open. The two furnaces treat in 24 hr. 50 tons blende concentrate reducing the S-content of Joplin blende from 31 to 0.5 per cent, consume in 24 hr. 350,000 cu. ft. gas, and require a 40-hp. motor. The depression in the furnace is sufficient to admit the air necessary for oxidation and to prevent SO_2 -gas from entering the building.

60. Muffle Furnaces, General.—In roasting finely divided suitable pyritic ores without the use of carbonaceous fuels the heat generated by the oxidation of Fe and S is sufficient to decompose sulphates formed, and the swelling of the ore permits oxidation to penetrate to the centers of particles. In addition, complete desulphurization is not usually required, although under favorable conditions pyrite with 50 per cent S furnishes a roasted product with 0.5 per cent S. The behavior of blende is different as shown in §49; the heat generated toward the end of the roast is not sufficient to oxidize remaining sulphide (± 8 per cent S) and to decompose the sulphate formed, hence extraneous heat has to be supplied. All furnaces near the discharge-end are therefore muffled, while at the feed-end, provided the kindling temperature prevails, and for one-half to two-thirds of the distance the ore has to travel the heat generated is sufficient for roasting to proceed without extraneous heat. The furnaces in use are therefore a combination of shelf-burners and muffles.

In a blende-roasting muffle a temperature of 800° to 900°C . is maintained in the hottest parts to decompose sulphates. Cold air entering the discharging muffle would reduce the temperature of muffle and ore, hence an excess of extraneous fuel would be required over that necessary when air is pre-heated; modern roasting furnaces therefore utilize the waste heat, which would pass off into the chimney, by conducting the oxidizing air through flues in the brickwork of the firing-end that it may take up some of the heat from parts where it is not needed, and return it to parts where it is most needed, *i.e.*, at or near the discharge-end. Preheating air in a separate furnace as in the Blake mechanical reverberatory roasting furnace¹ has not been successful economically. It is desirable for a satisfactory roast that blende of suitable size be brought quickly to

¹ *Tr. A. I. M. E.*, 1892-93, XXI, 943.

the ignition temperature; that the ignited blende have an abundance of fresh air and be frequently rabbled; that the partly roasted blende be held at a temperature of $850^{\circ}\text{C}.$, receive pre-heated air, and be frequently rabbled; that for the conservation of fuel, the outside furnace walls radiate little heat and the arches of the roofs be low; and that the amount of flue dust formed be small. As long as it is difficult to eliminate the S from blende to the required degree, furnaces which are raked by hand are maintained in many smelteries in spite of their great cost of labor and small tonnage when compared with furnaces rabbled mechanically. They have, however, the advantage that the operation can be readily changed to suit the ore under treatment so as to obtain a product which meets the requirements of the retort. As regards the air required for roasting in a muffle furnace, Rissman¹ states that flotation concentrates which were roasted with a great excess of air and long enough to retain as little S as 0.5 per cent, gave a product which did not work as well in the retort as the one obtained with less air and retaining 2.5 per cent S.

61. Muffle Furnaces Raked by Hand.—The first furnace² constructed to utilize at least part of the SO_2 for the manufacture of H_2SO_4 was the one erected by

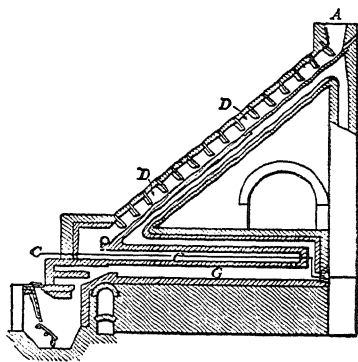


FIG. 56.—Hasenclever-Helbig furnace.

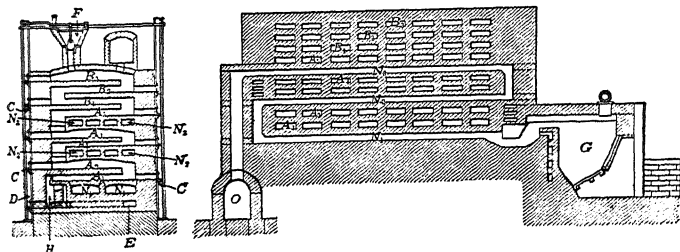
Hasenclever-Helbig in 1874, shown in Fig. 56.³ It consists of a reverberatory furnace *G* (18 ft. 9 in. long, 6 ft. 4 in. wide, 16 in. high) with superposed muffle *C* (21 ft. 4 in. long, 6 ft. wide, 16 in. high) ending in an inclined shaft *D* (29 ft. 6 in. long, 6 ft. wide, 20 in. deep) slanting at an angle of 43 deg. The flame of the reverberatory furnace from the adjacent gas producer heats the muffle and then the floor of the inclined shaft. The ore fed at *A* passes down the shaft in which its travel is regulated by transverse baffles *D* and a feeder at the lower end; it is then spread by hand in the muffle through side doors, and dropped from the latter on to the hearth of the reverberatory furnace and

¹ Ingalls, *Eng. Min. J.*, 1919, CVII, 87.

² Schütz-Hahn, *Eng. Min. J.*, 1912, XCIII, 557.

³ *Eng. Min. J.*, 1912, XCIII, 557.

worked similarly until the roast is finished. The furnace roasted in 24 hr., 4 tons of blende with 27 per cent S, required 1,120 lb. coal and five men. The S-content was reduced in the shaft to 8 per cent, in the muffle to 6 per cent, and in the reverberatory to 2.55 per cent. The shaft and muffle gas contain 5 to 6 per cent vol. SO_2 ; 50 to 60 per cent of the S is converted into H_2SO_4 . The furnace is not in use at present.



FIGS. 57 and 58.—Eichhorn-Liebig furnace.

In 1882 Eichhorn-Liebig patented their furnace in which all the S is utilized in the manufacture of H_2SO_4 and the S-content with siliceous ore reduced to 0.5 per cent; the furnace treated in 24 hr., 4 tons blende and required 1,600 lb. coal. It is shown in cross-section in Figs. 57 and 58.¹ In it A_{1-5} are hearths about 7 by 35 ft. heated by ducts N_{1-3} through which pass hot gases from an adjacent producer; B_{1-3} are similar hearths not heated; air for oxidation is admitted at D and heated in passing through E by the hot gases in N_1 . The blende is dropped at F on to B_3 , is rabbled and transferred through doors C and discharged through H ; the SO_2 -gas passes off through the flue over B_3 . In transferring the ore from hearth to hearth, it is pushed and drawn, and not moved sideways as is the case in most reverberatory and muffle furnaces. This furnace is little used at present.

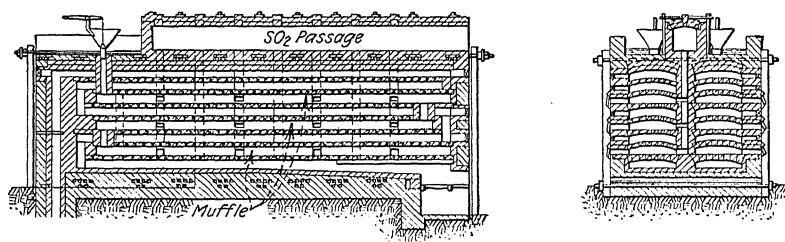
In 1886 Hasenclever built at Aix-la-Chapelle, Prussia, the Rhenania Furnace shown in Figs. 59 and 60² which is in operation in many European works. It has undergone a number of changes and has been abandoned by several plants, *e.g.*, in Belgium³ on account of its high fuel consumption and the difficulty of rabbling and transferring the ore. The furnace has three superposed muffles (40 ft. 8 in. long, 5 ft. wide, 9 in. high at center and 5 in. at side)

¹ Eng. Min. J., 1912, XCIII, 557.

² Eng. Min. J., 1912, XCIII, 558.

³ Nemes, *Metallurgie*, 1912, IX, 516.

connected with one another which are heated with coal from a fireplace beneath one end of the lowest muffle. A muffle has 10 working doors on a side. Two furnaces are combined to a block. The ore, fed on the top hearth, is rabbled and moved sideways by hand through side doors until it arrives on the bottom hearth from which it is discharged. The air necessary for oxidation enters through the working doors, the SO_2 -gas with 5 to 6 per cent vol. SO_2 from two furnaces is collected in a main flue leading to the Glover tower. At one time it was withdrawn from the several



FIGS. 59 and 60.—Rhenania furnace, Aix-la-Chapelle.

muffles through ports at the back leading into a vertical duct ending in the main flue. One side of a double furnace treats in 24 hr. 4 to $4\frac{1}{2}$ tons blende, reduces the S-content with siliceous gangue from 28 to 0.2 per cent, with calcareous gangue to 2 to 3 per cent, consumes 20 to 25 per cent coal, is served by two men on a 12-hr. shift. Hommel¹ proved experimentally that a capacity of 6.5 tons blende with 12-hr. shifts can be increased to 9 tons with 8-hr. shifts, thus showing the importance of frequent rabbling. The progress of desulphurization is shown by three examples² in Table 23.

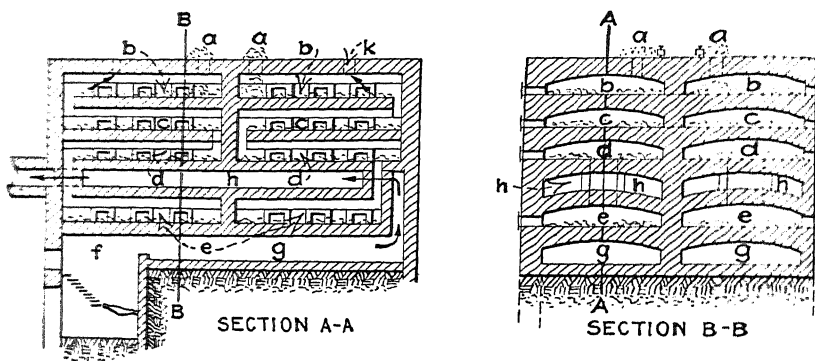
TABLE 23.—PROGRESS OF DESULPHURIZATION IN A RHENANIA FURNACE

Sample	I Sulphur, per cent	II Sulphur, per cent	III Sulphur, per cent
Crude ore.....	19.2	26.8	26.5
After 1st muffle.....	17.6	19.1	15.4
After 2d muffle.....	12.0	11.2	9.9
After 3d muffle.....	3.4	1.02	0.75
Roasted ore.....	0.6	0.35	0.75

¹ *Metallurgic*, 1912, IX, 281; *Eng. Min. J.*, 1912, XCIV, 697, 752.

² *Rev. Un. Min.*, 1890, IX, 18; *Berg. Hüttenm. Z.*, 1890, XLIX, 171; *Min. Ind.*, 1893, II, 649.

The first important change in the original furnace was that only the lower muffle was heated; the second that a cross-partition was erected dividing the long muffle (40 ft. 8 in.) into two smaller (20 ft. 4 in.) and thus affecting an increase in capacity and a saving in labor.¹ The two improvements are shown in Figs. 61 and 62 which give two sections of the furnaces in operation at the Guido works, Silesia. The flame from a step-grate travels through flues *a, b*, to the chimney. The ore dried on the roof of the furnace and fed at *a*, is rabbled and moved over the hearth *b, c, d, e*, the SO_2 gas passes off at *k*.



FIGS. 61 and 62.—Rhenania furnace, Guido works.

Peterson² has improved the heating of the bottom muffle.

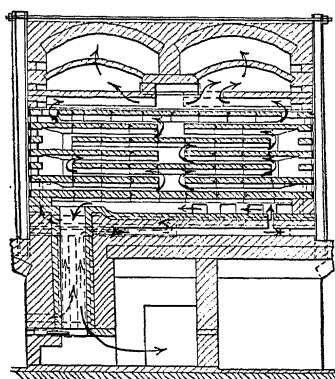
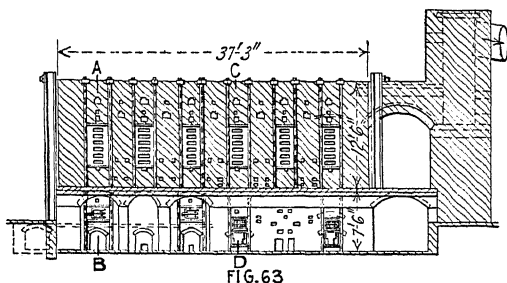
In working a Rhenania furnace, a charge of 1,000 tons of ore is dropped on one side on to the top hearth every 6 hr. and spread in front of three doors to a thickness of 8 in., after 6 hr. it is transferred to the second hearth and spread to a thickness of 6 in. in front of four doors, and again after 6 hr. to the lower hearth to a thickness of not over 4 in. in front of five doors. It often takes 8 hr. to finish a charge on the bottom hearth, the ore being tested for sulphide by heating with HCl in the presence of Zn and paper soaked with lead acetate. The ore thus remains 24 hr. in the furnace. The SO_2 gas with 6 to 7 per cent vol. SO_2 leaves the furnace with a temperature of 400°C . The temperatures in the muffles vary with the S-content of the ore, in the top muffle from 580° to 690°C ., in the second

¹ *Berg. Hüttenm. Z.*, 1893, LII, 339.

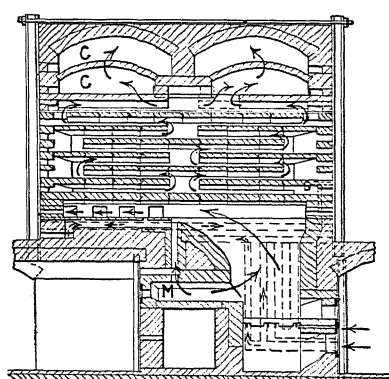
² *Metallurgie*, 1908, V, 701; *Eng. Min. J.*, 1912, XCIII, 559.

and third muffles from 750° to $900^{\circ}\text{C}.$ ¹ Mechanical rabbling and transferring of ore has been a failure.²

About 1888 Deplace³ constructed his first muffle furnace; the form of 1912 is shown in cross-sections and in elevation in Figs. 63 to 65. It is finding much favor in Europe on account of its many advantages over the Rhenania furnace which had become the



Section A-B
FIG. 64



Section C-D
FIG. 65

FIGS. 63, 64 and 65.—Deplace furnace.

standard. The furnace resembles the well-known double Maletta shelf-burner⁴ with this difference that the bottom shelf and the roasting air are heated. The elevation shows a block of six burners,

¹ *Rev. Un. Min.*, 1890, IX, 18; *Berg. Hüttenm. Z.*, 1890, XLIX, 171.

² *Berg. Hüttenm. Z.*, 1893, LII, 43.

³ Guillet, *Mém. & Compt. rend. travaux Soc. Ing. Civ. de France*, 1911, I, 758.
Lummen, *Eng. Min. J.*, 1916, CI, 1021, CII, 741.

Nemes, *Metallurgie*, 1912, IX, 516.

⁴ Hofman, "Copper," 1918, p. 89.

37 ft. 6 in. long, 23 ft. wide and 20 ft. high, with six burners and four fireplaces, of which two serve three burners. A burner has seven shelves, 4 ft. $7\frac{1}{8}$ in. wide, 3.189 in. thick, roasting spaces are $6\frac{1}{2}$ in. high. The blende in its downward path travels a distance of about 41 ft. The fireplace is a combination of retort and grate. The retort *M* is charged with coal, and heated by waste-heat flues and by radiation from the deep grate, the de-gasified coal is pushed on to the grate; the volatile H-C is burned by pre-heated air and by the excess air in the products of combustion of the coke fire. The flame from a fireplace travels under the bottom shelf, just above, and enters the heating flues of the neighboring shelf, returns, descends in flues at the end of the fireplace and gives off heat to the incoming air for roasting, which is brought to a temperature of 700°C . On the sides of the fireplace are air-flues which furnish hot air for the combustion of the volatile H-C. The temperature of the heating flame reaches $1,100^{\circ}$ to $1,200^{\circ}\text{C}$. The rabbling doors at the front and back of the furnace are just large enough to admit the rabble-head 12 by 1.5 in. It will be noted that, as in the Eichhorn-Liebig furnace, Figs. 57 and 58, the ore is pushed and drawn on the hearth and not moved laterally. A unit roasts about 2,200 lb. blende in 24 hr. with a fuel consumption of 10 per cent, and furnishes gas with 6.5 to 7 per cent vol. SO_2 . A laborer empties the lowest hearth of his unit every 4 or 6 hr., brings down ore from the upper hearths, and charges the top hearth with 180 to 250 lb. blende; he rabbles the ore once an hour or once in 2 hr. Much skilled labor is required for the work; the furnace is low-priced and does very efficient work; the amount of flue dust formed is very small. Blocks contain 6, 9, 12, and even 18 burners.

62. Muffle Furnaces, Raked Mechanically.¹—The high cost of labor and the small capacity of hand-rabbled muffle-furnaces have prompted the application of machinery to replace manual labor. A mechanical furnace has the disadvantage that the original cost is high, that the roasted ore is discharged whether the S has been eliminated satisfactorily or not (high-S product has to be re-treated) and that the amount of flue dust formed is likely to be high. Euro-

¹ Schütz, *Metallurgie*, 1911, VIII, 653, transl. Hahn, *Eng. Min. J.*, 1912, XCIII, 557; 1915, XII, 109.

Hommel, *Metallurgie*, 1912, IX, 281, transl. Hahn, *Eng. Min. J.*, 1912, XCIV, 697, 752.

De Lummen, *Eng. Min. J.*, 1916, CI, 1021; CII, 741.

Chase, *Eng. Min. J.*, 1917, CIV, 698.

pean works with low-priced labor adhere to hand furnaces; in the United States there are in operation only a few hand furnaces, and the Hegeler furnace, condemned by Europeans, was the only mechanical furnace in operation until the Spirlet came into use. In 1915¹ the 35 muffle furnaces were all of the Hegeler type.

The mechanical furnaces have either stationary or moving hearths. In the first class the hearths are either straight-line (Brown, Saeger-Brown, Hegeler, Ridge, Merton, Falding) or circular (Hommel, Haas, McDougall, Zelewski); the rabbles move longitudinally or are rotated being attached to revolving vertical shafts. In the second class the hearth is either a revolving cylinder (cone) or a circular horizontal plate; the rabbles with the latter are either fixed in the roof (Stolberg) or attached to the hearth (Spirek). On the whole multiple-hearth furnaces are the rule.

63. Brown Furnaces.—The Brown² and Saeger-Brown³ muffle furnaces are single-hearth furnaces of great length, 150 and 328 ft., which have been built in two instances and again abandoned, as their tonnages were small and the fuel consumption excessive. They bring out strikingly the defect of having a high arch (25 in. with Brown) and of suffering considerable loss of heat by radiation through the roof.

64. Hegeler Furnace,⁴ Figs. 66 and 76.—This furnace was erected in 1882 at the works of the Mathiessen & Hegeler Zinc Co., La Salle, Ill. It has undergone many changes from the original form, so that at present it represents rather a type than a definite structure. It consists of a rectangular brick block 80 ft. long, 17 ft. wide and 22 ft. high which contains two compartments separated from one another by a vertical partition; each compartment has seven staggered arched hearths, 6 ft. wide, over which the ore fed on the top shelf is raked mechanically by means of rabble-frames pulled by steel rods, until it is discharged at the bottom; the roaster gases travel in the opposite direction. The three lower hearths are muffles which are heated from an extraneous fireplace. The open ends of the hearth are closed by tilting doors, Fig. 66, for the ingress and egress of the plows and rods, and for the discharge of the ore from the bottom muffle. The length and width of a hearth, which used to be 40 ft. and 4 ft. 6 in., has been increased to 60 ft. and 6 ft.,

¹ *Eng. Min. J.*, 1915, XCIX, 421.

² Ingalls, "Zinc and Cadmium," p. 139.

³ *Eng. Min. J.*, 1912, XCV, 753.

⁴ Mühlhaeuser, *Eng. Min. J.*, 1910, XC, 314.

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and the roasting capacity in 24 hr. advanced from 30 tons to 50 tons of blende concentrate not exceeding 2 mm. in size.

Figures 66 and 67 represent a general plan and Figs. 68 to 70 vertical cross-sections and an elevation of one of the furnaces in operation at Donora, Pa. The seven-hearth furnace (80 ft. long, 17½ ft. wide, 22 ft. 1 in. high outside) has at either end a seven-stage turntable, 10 by 14 ft., and a corresponding rod alley, 126 ft. 2 in. long, to receive the rabble-frames pulled through the furnace and the steel drawing rods attached to a sprocket chain driven by a 35-hp. motor. On one side of the north rod alley is a water-seal

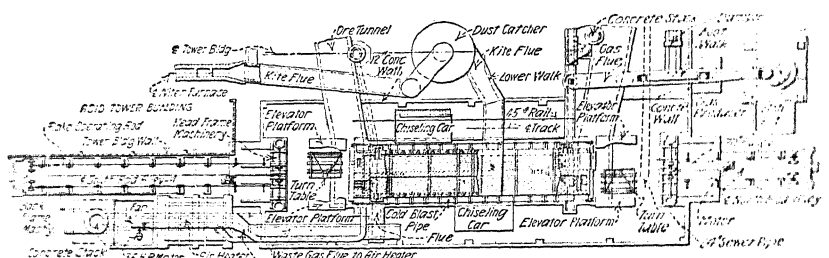


FIG. 66 GENERAL PLAN

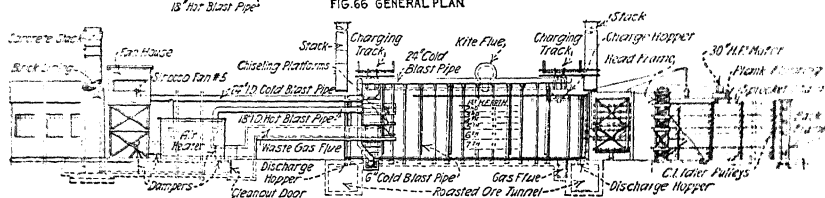


FIG. 67 SIDE ELEVATION

FIGS. 66-76.—Hegeler furnace.

mechanical 10-ft. gas producer worked with forced draft. The horizontal branch of the flue leading the gas to the kiln has on the upper side doors to permit blowing out of dust and removing soot. The gas descends, is admitted to the bottom of the heating flue (1st gas, Fig. 70) where it meets air under pressure and burns. The flame travels underneath the seventh hearth to the opposite end, rises in a side pass to the second heating flue (2d gas), travels here in the opposite direction, rises through the side pass, shown in Fig. 70, to the top heating flue (3d gas), leaves the furnace at the end of the third gas flue, and enters the waste-gas flue, Figs. 66 and 67. The flue conducts the hot waste gas into the air heater which has the form of a pipe-stove. Having given up a part of its heat, the waste gas enters the concrete stack, 110 ft. high, 5 ft. 1 in. in diameter,

SMELTING OF ZINC ORES

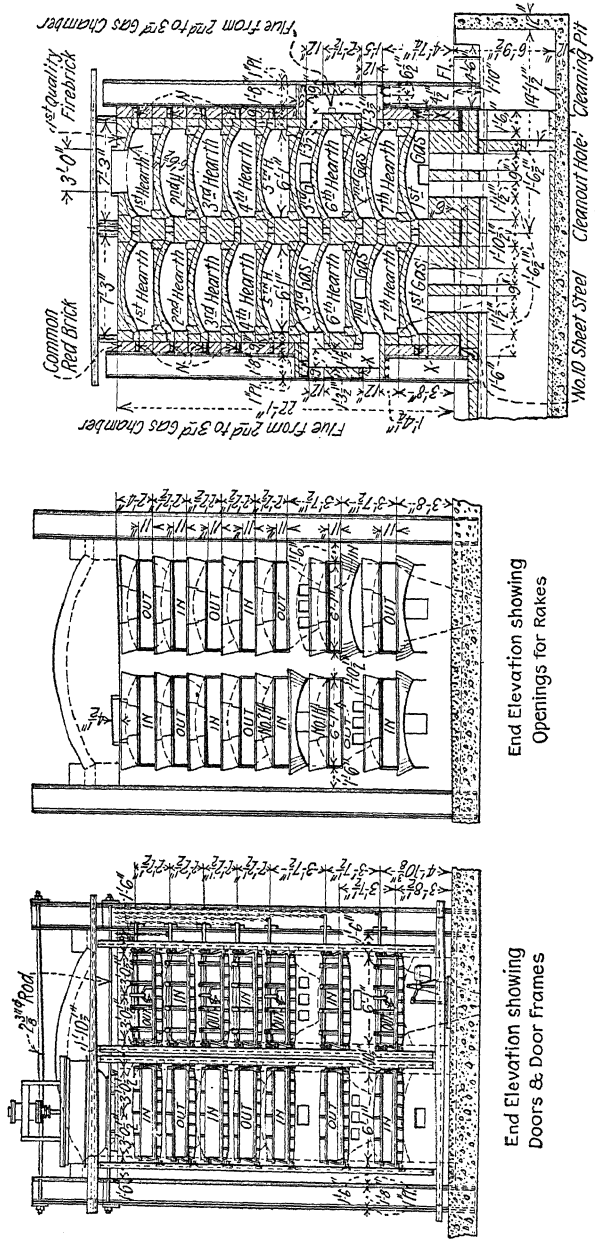


FIG. 68.

FIG. 69.

FIG. 70.

lined with 5-in. brick for a height of 55 ft. In the front of the stack is the fan house with a No. 5 Sirocco fan driven by a 35-hp. motor at 1,050 r.p.m., which delivers into a 24-in. cold-blast pipe and furnishes the air necessary for running the gas producer and burning the producer gas. Near the fan there branches from the 24-in. cold-blast pipe a 15-in. pipe leading into the pipe-stove air heater. The hot air leaves the heater through an 18-in. pipe which delivers into 8-in. zigzag pipes, Fig. 64, beneath the first gas flue Fig. 70 whence the air having taken up additional heat enters well pre-heated the bottom or seventh hearth, Fig. 70. If the air heater is not used, the waste gases from heating the muffles pass off into a steel stack, 4 ft. 6 in. in diameter, near the end of the furnace;

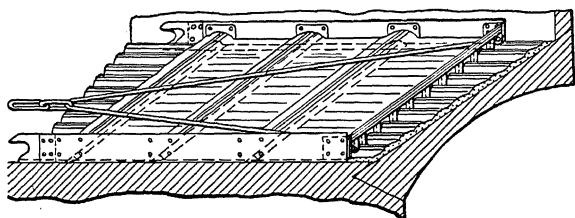


FIG. 71.

the air necessary for roasting is pre-heated by being drawn through the 8-in. pipes, Fig. 66, beneath the first gas flue, Fig. 68. In most furnaces the 8-in. zigzag pipes are replaced by straight-line flues. In the division wall, Fig. 66, which separates the two kilns, are ports to admit cold air to the upper hearths in case these should be too hot or suffer from a lack of oxygen. The roaster gases are withdrawn from the top hearth by the steel kite flue, Figs. 66 and 67, 6 ft. 9 in. in diameter, lined with 2 in. of magnesia, and delivered into the steel dust catcher, 22 ft. in diameter; they leave it through a pipe 6 ft. 9 in. in diameter, lined with 2 in. of magnesia, and enter the niter furnace of the sulphuric acid chamber. Figure 66 shows in addition two chiseling cars each with three platforms, Fig. 65, and two elevator platforms at each end of the furnace; Fig. 65 represents also charging tracks and ore hoppers. The chiseling car has been replaced by a steel frame running on a track and guided at the top by flanged wheels; the frame has a movable platform driven by a motor attached to the top horizontal member; it is pushed by hand along the side of the furnace.

The rabbling of the ore and its mechanism form characteristic features of the furnace. The rabble-frames are very much alike. Figure 71 gives a perspective view. The frame resembles a sled, with two side bars as runners, four crosspieces of which three serve as cutter bars and one as rake bar, and one V-shaped haulage rod with two chain links.

The details of the frame in use at Langeloth, Pa., are shown in Figs. 72 and 73. It is 9 ft. long and 5 ft. $10\frac{5}{8}$ in. wide; has two side

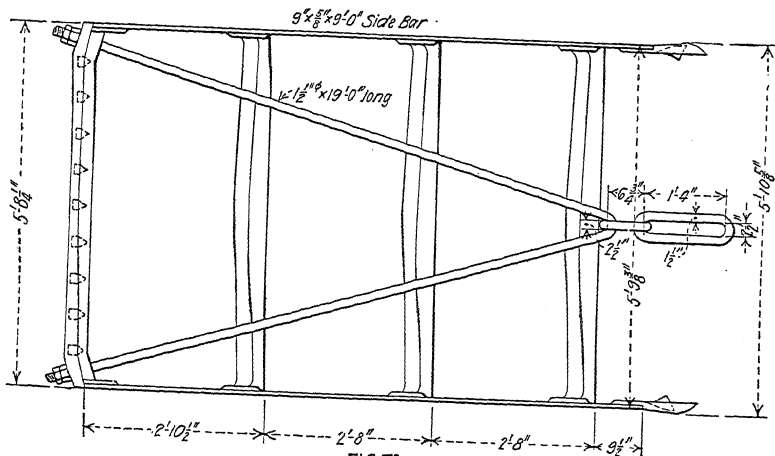


FIG. 72

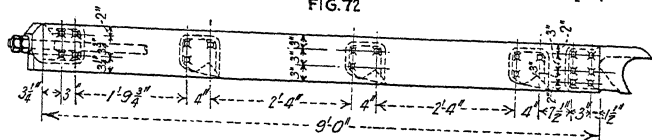
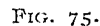


FIG. 73

bars, 9 ft. by 9 in. and $\frac{5}{8}$ in. thick, which glide on shelves $\frac{3}{4}$ to 1 in. high, Fig. 68, forming parts of the side walls of the hearth, and thus keep the blades of the rake bar from the floor; the side bars have side cutters to remove ore banked on the side shelves or adhering to the wall.

The three cutter bars are of triangular steel $3\frac{3}{4}$ in. at face, $3\frac{3}{8}$ in. at back, 5 in. at base, forming an angle of 53 deg. with the horizontal; they are bolted to the side bars, dig into the ore, push part of it forward while the rest passes over the ridge and drops back on to the hearth. The one rake bar has nine V-shaped blades which turn over the ore after it has passed the cutter bars. The V-shaped haulage rod is $1\frac{1}{2}$ in. round iron; and the two chain links to be slipped

A furnace requires seven rabble-frames and 14 rake bars about 112 ft. long, *i.e.*, they extend from the furnace-side of one turntable through the furnace to the head frame of the opposite rod alley.



The rabbling mechanism, Figs. 66 and 67, is contained in the two rod alleys, one at either end of the furnace. An alley is a steel structure with idler pulleys carrying the rake bars which are temporarily attached to sprocket chains passing over sprocket wheels in the back and head frames. In the head frame is located the driving mechanism. Power, derived from a 35-hp. motor, is transmitted through an intermediary pulley by open and cross belts to a central 30-in. tight pulley which has on either side a loose pulley. The horizontal shaft of the central pulley at Langeloth, Pa., Fig. 74, has at either end a Hill clutch; these are made to engage with one

This architectural drawing shows a symmetrical facade with a central entrance and two side entrances. The central entrance features a large, arched window above the door. The side entrances are flanked by large, arched windows. The drawing includes various dimensions in feet and inches, such as 8' 1/2", 3' 4", 10' 1/2", and 14' 10". The drawing is oriented vertically on the page.

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) = \frac{\partial L}{\partial x}$$

The Blende for the kiln, coarse and smaller and dry, is fed on to the top hearth of a compartment either by a separate feeding device or by the rabble frame when it passes beneath the discharge hopper holding the desired amount of ore. The rabble frame, on the top of first shelf of the turntable near the feed end, is hooked to the rake bar which had been passed from the opposite head frame and through the furnace and guided in its path by a central channel iron in the

turntable, pulled over the hearth, and delivered on the corresponding shelf of the turntable at the opposite end. While the frame glides through the furnace with its side-bar runners, it travels in the turntable on four pairs of rollers, between which is the channel iron for the guidance of the rake bar. At the ends of the roller paths are stops which prevent the carriage from being pulled too far. Part of the ore on the upper or first hearth has been dropped through the discharge port at the end of the second hearth. The frame on the second shelf of the nearby turntable is hooked to the drawbar, which had been passed from the opposite head frame through the furnace, pulled over the second hearth and delivered on to the second shelf of the turntable at the opposite end, and so on, until the roasted ore is discharged from the seventh hearth into a car in the roasted-ore tunnel.

The ore for the other compartment is fed at the opposite end from that of the first. The turntables, having been used for receiving the rabble-frames from one compartment, are turned 180 deg. and do the same service for the other. A compartment is usually raked every 2 hr. In some plants with ores that give up their S readily, a compartment is raked every 1 hr. 10 min., in others every 1 hr. 25 min.; the more frequent rabbling the greater the tonnage above the usual 40 tons. The ore passes through a compartment in about 36 hr. Changes in temperature on hearths are shown by three examples in Table 24.

TABLE 24.—TEMPERATURES OF ORES IN PASSING THROUGH KILN

Hearth No.	1	2	3	4	5	6	7
Temperatures °C.....	798	827	775	771	715	825	705
Temperatures °C.....	788	823	780	791	772	843	834
Temperatures °C.....	772	802	796	769	797	794	818
Average.....	786	817	784	777	761	821	786

The temperatures, averaging 786° on hearth 1 rise to 817° on hearth 2, then fall on hearths 3 and 4, rise again on hearths 5, 6 and 7, which are treated by extraneous fuel.

In some plants the hearths of the two compartments are raked together, *i.e.*, hearth 1 in compartment *A* is raked, then hearth 1 in compartment *B*; the operation is repeated on hearths 2 of compartments *A* and *B*, and so on.

The different parts of the mechanism are managed at the furnace ends through chains running over pulleys. For hooking and unhooking rake bars, the operator stands on a balanced platform, Figs. 64 and 65. Two men attend to the working of a furnace in an 8-hr. shift, they deliver raw and remove roasted ore. In some plants provided with special devices, *e.g.*, that of the J. J. Simmonds Engineering Co., Lawrence, Kan., the rabble-frames are manipulated by a single man. In addition to the labor required for manipulating the rabble-frames, a furnace is served by 12 to 18 men in 24 hr. for chiseling, cleaning up, repairing, etc.

Heating the muffled hearths by having a flame zigzag upward has caused much trouble, as deposits of soot and dust have interfered with uniform heating; further, there is little control of temperature. It is for this reason that in a number of kilns parallel firing has been installed, *i.e.*, the flues are heated severally, the products of combustion combining in a main flue leading to a stack. In some plants Siemens regenerators have been placed under the furnace for pre-heating producer gas and air. A cross-section of the regenerators, combustion chambers and three ore hearths of Pueblo, Colo., is shown in Fig. 76. Gas and air ascend in one pair of regenerators and meet in the horizontal combustion flue; the flame ascends in a vertical flue parallel with the side walls; from the flue three tiers of 5-in. ports (four between a pair of buckstays) conduct the flames into the three combustion chambers of one compartment, pass through ports in the central division wall into the combustion chambers of the other compartment, leave these through corresponding ports, descend in a vertical flue, and enter the other pair of regenerators. Every half to three-quarters of an hour gas and air currents are reversed. Opposite each 5-in. port is an opening in the outer wall, closed by a brick, to furnish access to the port for removing dust or reducing the temperature. This method of heating the muffles is very satisfactory. In a new furnace the regenerator chambers would be made 5 ft. high instead of 2 ft. 11½ in., as in Fig. 76, and the gas channels beneath 30 in. high instead of 18 in.

A furnace roasts 40 tons dried ore, the ore forming a layer 4 in. deep, reduces the S-content to 2 per cent; consumes 1.34 tons of moist or 1 ton of dry coal per ton of ore; makes 50 lb. dust per ton of ore; two men are in attendance in an 8-hr. shift; two to three men cut out leady hearth accretions, they clean a hearth in 8 hr. The roaster gas contains about 4 per cent vol. SO_2 .

The Hegeler furnace is cumbersome but it is the only one which has capacity; the cost of the furnace before the war was \$50,000, the cost of roasting in 1913 was about \$2.25 per ton, at present it is about \$4.50.

The S-content of the ore is not reduced below 2 per cent, as the roasting operation has to be governed by the working of the acid chamber which demands a uniform volume of gas of definite temperature and SO₂-content; and this requirement is difficult to meet if the percentage of S in the roasted ore is to be brought down to a lower figure.

Special reasons must have prompted to use the Hegeler kiln as a reverberatory furnace as is the case at Port Pirie, N. S. W., where the three lower muffles have been changed into reverberatory hearths. The furnace is fired from two Duff gas producers, the flame zigzags upward over the seven hearths.

65. Ridge Furnace.²—This is a straight-line five-hearth furnace 56 ft. long. It is shown in Figs. 77 to 79. The top hearth, Figs. 77 and 78, serves for drying and pre-heating the ore, the three following for roasting it, and the bottom hearth for cooling the roasted ore and warming part of the oxidizing air. The bottom hearth is heated from a fireplace, shown in Figs. 77 and 78; the fire gases traveling through square flues, Fig. 79, heat the floor of roasting hearth No. 3 and the roof of the oblong flues carrying part of the oxidizing air. The air, warmed by passing above and underneath the roasted ore, enters the roasting hearth No. 3 and zigzags upward in a direction opposite the travel of ore; it leaves the top hearth by a gas flue as SO₂ gas which goes to the Glover tower. The rabbling mechanism is similar to that of the Edwards reverberatory furnace.³ It is made up of four water-cooled revolving shafts, each of which carries five radial arms provided with teeth at the proper angle. The ore, fed at one end of the drying and pre-heating hearth, is moved by the rabbles to the other, where it drops through a port on to No. 1 roasting hearth; it is made to travel in a similar manner over hearths Nos. 2 and 3, and meets at the end of the latter the pre-heated oxidizing air; from hearth No. 3 the roasted ore drops on to the cooling hearth over which it is rabbled

¹ *Min. Mag.*, 1914, X, 66.

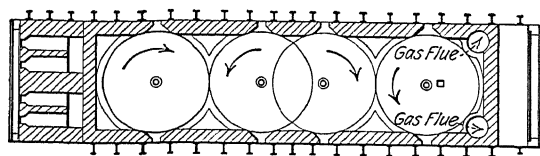
² Ridge, *Eng. Min. J.*, 1917, CIII, 315.

Case, *op. cit.*, 1917, CIV, 688.

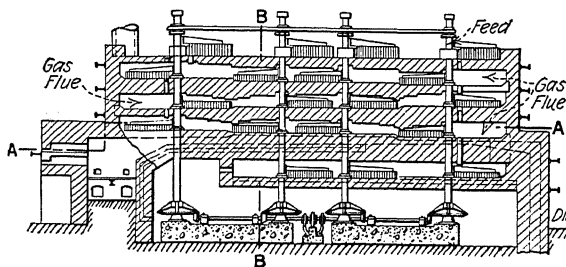
Ridge, *Met. Chem. Eng.*, 1917, XVII, 215.

³ Hofman, "Copper," 1918, p. 116.

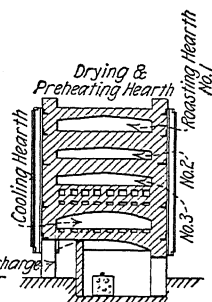
to the discharge opening. The oxidizing air entering at one end of the cooling hearth, passes over the ore and takes up the heat contained in it. The coking method of firing is employed to obtain a smokeless flame. It will be noted that the ore is rabbled continuously, that the arches are low so that the gas current carries with it the SO_2 set free, that the air is pre-heated, that the exchangeable rabbles are accessible through sidedoors (not shown), that the driving gear has a solid foundation and is in a cool place and protected from dust. The furnace cost \$15,000 erected in England



Longitudinal Section
FIG. 77



Section A-A
FIG. 78



Section B-B
FIG. 79

FIGS. 77, 78 and 79.—Ridge furnace.

before the war, requires $\frac{7}{8}$ hp. and some cooling water, treats from 12 to 14 long tons of ore in 24 hr., reduces the S-content of good ores to 0.5 to 0.6 per cent.

The Falding furnace¹ resembles the one of Ridge.

66. Merton Furnace.—The first Merton furnaces were three-hearth reverberatory furnaces² which used the Edwards mechanism for rabbling and moving the ore. Later, the furnaces were muffled. In 1917 there were in operation duplex three-muffle³ and six-muffle furnaces.⁴ In them the ore, fed at one end of the top muffle, is

¹ Ingalls, "Zinc and Cadmium," p. 141.

² Hofman, "Copper," 1918, p. 121.

³ Ridge, *Met. Chem. Eng.*, 1917, XVII, 215.

⁴ Chase, *Eng. Min. J.*, 1917, XIV, 698.

made to travel to the other, when it drops on to the second, is moved in the opposite direction, and so on until it arrives at the discharge; the oxidizing air is pre-heated by passing through flues surrounding the firebox. The latest furnace¹ differs from the earlier types in that it has on top a drying hearth followed by three muffle hearths, one reverberatory furnace and one cooling hearth, and that in a block the superposed hearths are worked in pairs. Figures 80 and 81² represent a block of two pairs of superposed hearths, with a

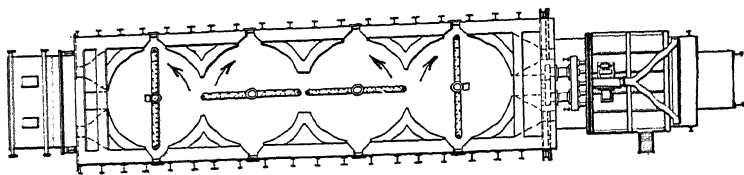


FIG. 80

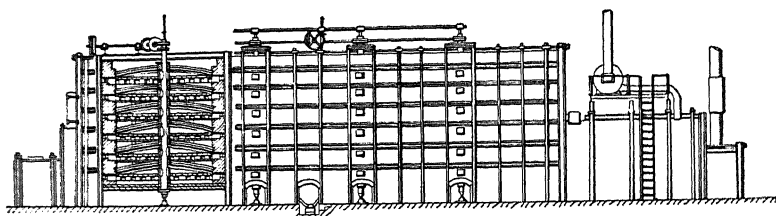


FIG. 81

FIGS. 80 and 81.—Merton furnace.

single fireplace at one end and the gas delivery at the other. The block has four water-cooled revolving shafts provided with rabble-arms and these with rabble-teeth; the shafts are driven at the top by gearing. The ore, fed at the junction of two hearths forming a pair, is rabbled spirally inward and discharged near the centers on to the two next hearths of the pair; here it is moved outward as in the well-known McDougall furnace, and zigzags downward until it is discharged from the cooling hearths. The ore-ports are separate from the gas-outlets so as to reduce the amount of flue dust carried by the SO_2 gases. The fuel gases which heat the bottom muffle and the reverberatory hearth are passed through a recuperator before they are delivered to the stack. The oxidizing air, moved by a fan, is pre-heated in a recuperator, and the heat

¹ Editor, *Eng. Min. J.*, 1918, cvI, 569.

² *Eng. Min. J.*, 1918, cvI, 569.

taken up by the air passing over the cooling hearth is returned to the furnace by entering the fireplace.

The disadvantages of the Ridge and Merton furnaces, judging by the behavior of the McDougall types, are that the shafts and rabble-arms, being constantly held at an elevated temperature, are short-lived and demand much repair; also that the water-cooled iron has a tendency to reduce temperature.

The Dohet furnace¹ resembles a Deplace furnace in which the ore is rabbled in a manner similar to the Spence pyrite burner.²

67. Circular Furnaces.³—Stationary circular furnaces with horizontal rabbling-arms attached to vertical revolving shafts, have the disadvantage that the diameters and therefore the roasting power cannot be large without making the distances between the hearths too great, while for the effective roasting of blende the distances ought to be small.

The Hommel furnace⁴ consists of a horizontal revolving hearth for rough-roasting blende and beneath it a stationary annular hearth on which the rough-roasted ore is to be dead-roasted, being moved by scrapers attached to the circumference of the revolving hearth

The Haas furnace⁵ is an improved Ross-Welter furnace.⁶ The ore, in four superposed connecting muffles heated from a single fireplace, is made to travel downward as in a McDougall furnace. It was installed at Oberhausen about 1885 but has been given up.

The McDougall furnace, of which the Evans-Klepetko, improved Herreshoff, and Wedge are the leading representatives has not found favor in dead-roasting blende for the reasons given above. It serves its purpose very satisfactorily in sulphatizing mixed blende concentrate previous to leaching with sulphuric acid, an operation in which the temperature does not exceed 700°C.

The Zelewski furnace⁷ is a combination of a three-hearth McDougall kiln discharging the rough-roasted ore into two adjacent heated finishing muffle furnaces in which the ore received at the center is moved by rabble-arms to the periphery to be discharged;

¹ Schütz, *Metallurgie*, 1915, XII, 109.

² Hofman, "Copper," 1918, p. 91.

³ Hommel, Haas, McDougall, Zelewski.

⁴ Hommel-Hahn, *Eng. Min. J.*, 1912, XCIV, 752.

⁵ *Berg. Hüttenm. Z.*, 1884, XLIII, 5; *Rev. Un. Min.*, 1894, XXV, 43.

⁶ Mahler, *Ann. Min.*, 1885, VII, 518.

⁷ Schütz-Hahn, *Eng. Min. J.*, 1912, XCIII, 557.

thus roughing and finishing roasts are carried on in separate but connected furnaces.

68. Revolving Cylinders.—Furnaces of this type have been put in operation at the works of Hemixem, Belgium,¹ and constructed by Schmieder² and perhaps others. The objections to this type of furnace are difficulties of construction and maintenance, thickness of layer of ore, small tonnage, as muffles cannot well have a large diameter.

Stolberg Furnace.³—This furnace resembles in its general features the Brunton or Godfrey reverberatory furnace⁴ excepting that the hearth is a muffle heated from three fireplaces. The furnace has a horizontal circular muffled hearth traveling on rollers, and a stationary roof with fixed rabble teeth. The ore, fed at the center strikes the fixed teeth, is turned over as the hearth revolves and moved gradually toward the periphery where it is discharged. The furnace is in operation at Münsterbusch, Germany, and appears to give satisfactory results.

69. Spirlet Furnace.⁵—This furnace, in operation in Belgium, Germany and the United States, is shown in half elevation and half-vertical section in Fig. 82. Its mechanical features differ somewhat from the European prototypes. The characteristics of the Spirlet furnace are that it is circular, has four superposed hearths with brick rabble teeth projecting downward, that two hearths rotate and two are stationary, and that the floor of the bottom hearth is heated. The dried ore, fed on the top hearth near the periphery, is moved by rabble teeth toward the central discharge opening, drops on to the second hearth, is moved outward, falls through twelve 3- by 9-in. ports near the periphery on to the third hearth, travels in the same manner on hearths three and four, and is discharged from the latter through two ports *F*, 10 by 10 in., into hoppers *G* closed by a swing gate. Pre-heated air moves over the hearths in a direction opposite to that of the ore, and leaves the roof of a furnace as SO₂ gas.

¹ Nemes, *Metallurgie*, 1912, IX, 516.

Schütz, *op. cit.*, 1915, XII, 109.

² *Min. Eng. World*, 1911, XXXV, 1,018; *Metallurgie*, 1915, XII, 109.

³ Schütz-Hahn, *Eng. Min. J.*, 1912, XCIII, 557.

⁴ Hofman, "Lead," 1918, p. 164.

⁵ Nemes, *Metallurgie*, 1912, IX, 516.

Schütz, *op. cit.*, 1915, XII, 109.

Ridge, *Met. & Chem. Eng.*, 1917, XVII, 215.

Harlow, *Eng. Min. J.*, 1918, CVI, 293.

The foundation is a rectangular brick block, 15 ft. 6 in. long, 6 ft. 6 in. wide, and 7 ft. 2 in. high. It contains the firebox *J* with flues *S* for warming its combustion air; two cast-iron downtakes, *M*, with radial iron fins, connected by cross flue *N* with the stack; two receivers *R* for roasted ore; one inlet *O* for roaster air pre-heated

LEGEND

- A- Green Ore Feeder
- B- 1st Ore Hearth (Ore Raked in)
- C- 2nd " " (" " out)
- D- 3rd " " (" " in)
- E- 4th " " (" " out)
- F- Ore Pass to Hopper
- G- Roasted Ore
- H- SO₂ Pipe to Main SO₂ Flue
- I- SO₂ Damper
- J- Fire Box
- K- Gas Uptake
- L- Combustion Chamber (Baffled)
- M- CO₂ Down-take (Fins Out Side)
- N- CO₂ Flue to Stack
- O- Air Intake
- P- Preheating Chamber
- Q- Air Uptake from P
- R- Air Register to Roaster
- S- Combustion Air

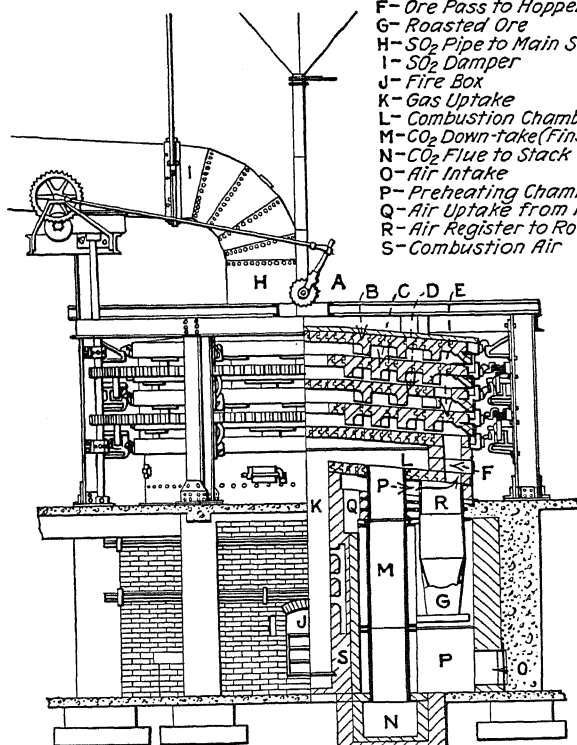


FIG. 82.—Spirlet furnace.

in chamber *P* and an uptake *Q* before it is delivered at 600°C. to the ore pass *F*—the speed of its travel being regulated by register *R*. The air muffle *P* is 8 in. high and is encased in the same cylinder as the combustion chamber *L*. The flame from the fireplace *J* reaches through a 32-in. firebrick uptake *K* the center of the combustion chamber *L* which is 12 in. high and baffled in order that its

roof, which is the bottom roasting hearth, may be uniformly heated. The furnace proper is 14 ft. in diameter. The roasting spaces are $6\frac{3}{4}$ in. high. The arched roofs are built of special tile, every alternate one being prolonged to form a rabble tooth which extends to within 1 in. of the floor. The roof is built in a steel ring 14 ft. in diameter, which is supported by lugs riveted to the periphery. The lugs of the fixed arches rest on hangers attached to the six columns of the steel framework. The hangers carry two rows of flanged wheels which support 90-lb. circular rails and serve to support the movable hearths through suspension members. To the outside of the rail are bolted 12 segments of cast semi-steel which form a toothed wheel with 300 teeth. A pinion meshes with the circular wheel and causes the hearth to make 1 rev. in 9 min. The dried ore, dropping from a hopper through a vertical pipe *U* into a ratchet-driven wormfeed *A*, is delivered onto hearth *B* about 3 ft. from the center and not at the periphery, in order that the gas current may deposit dust in the space between ore and periphery; the dust will be rabbled into the ore when it has reached a thickness of 1 in.; in this way most of the dust is returned to the furnace. Both stationary and moving hearths have ore-seals carried in annular troughs enclosing the peripheral bands. The SO_2 gas is withdrawn from the roof near the periphery through the 30-in. brick-lined uptake *H* which has an inner diameter of 24 in.; the uptake has a cut-off damper *I* and rises at an angle of 30 deg. in the main flue.

Accretions and scale which form are loosened or chiseled off through 4- by 6-in. side doors, 12 to a hearth, and carried out by the rabble teeth. When teeth are worn or broken, the furnace is shut down, the hearths are hoisted and removed by a three-legged spider attached to a 5-ton hand-operated differential chain block which is suspended from a traveling crane also operated by hand. New hearths are put in to replace those that are defective without cooling the furnace. The furnace requires 2 hp. for running and 3 hp. for feeding; it treats in 24 hr. 7,800 lb. green ore and 1,800 lb. spill, or 9,600 lb. of ore, requires 1,400 lb. or 15 per cent coal, and one man per shift. The ore can run as low as 25 per cent S but 26 per cent is preferable. The roasted ore retains 0.5 to 0.8 per cent S; the SO_2 gas contains 7.5 per cent vol. SO_2 , its tenor varies only a few tenths of 1 per cent; the SO_2 -content can be run up to 10 per cent, but this is not conducive to a good roast. The life of the furnace under the most favorable conditions is about 1 year. Ordinarily the upper hearth lasts from 4 to 6 months, and the bottom

hearth from 6 to 8 months. The reason for this is the necessity of chiseling crusts which form on the upper hearth. At first the life of the rabble teeth was rather short, and prompted trials with alundum teeth having cast-iron centers; but with strong hard firebrick the teeth last as long as the hearth. It has been found that Montana black blende concentrate which contains associated pyrite roast better than rosin colored Joplin concentrate free from pyrite.

70. Blast Roasting.—This process which is working successfully in partially roasting and agglomerating sulphide lead and copper ores has been proposed for treating blende.

The works of Stolberg¹ have patented a furnace for this purpose. It is a circular furnace with perforated cast-iron plate serving as a grate which carries a layer of crushed limestone; in the center is a hollow rotating shaft with two rabble arms provided with teeth. Air warmed by passing through the shaft and arms is delivered beneath the grate and roasts the ore spread on the bed of limestone.

Kessler² has patented a heated vertical brick cylinder with revolving vertical screw conveyor and a bottom blast-inlet pipe; the ore heated to the ignition point is to be roasted during its passage through the furnace.

Fulton³ has developed a new method for roasting finely developed blende, especially flotation concentrate, by mixing the ore, preheated to 60° to 100°C., with air under a pressure of 20 to 80 lb., and blowing the mixture into a cylinder where it comes in contact with air under pressure heated to 800°C. The blende is roasted instantaneously; the bulk of the ore is collected in a chamber, and the impalpable dust in a Cottrell precipitator. Experiments with a complex flotation concentrate containing 31.4 per cent S, 44.3 Zn, and 11.6 Fe, gave a product with 2.2 to 3.6 per cent S. It is estimated that the total cost of roasting a ton of ore will be \$1.40.

Finishing rough-roasted ore in a Dwight-Lloyd machine has been noted on page 82.

71. Fire Concentration (Zinc Burning).⁴—The usual process of smelting zinc ores with an admixture of about 50 per cent reducing fuel in a retort of not over 10 in. in width demands that the ore be

¹ Schütz, *Metall u. Erz*, 1915, XII, 110.

² *Loc. cit.*

³ Fulton-Read, *Eng. Min. J.*, 1920, CX, 405.

⁴ Ingalls, *Min. Ind.*, 1912, XXI, 893.

Clerc, *Eng. Min. J.*, 1912, XCII, 127; 1913, XCV, 222.

Ingalls, *Tr. A. I. M. E.*, 1917, LVII, 696.

high grade. Low-grade ores are usually enriched by water concentration, frequently supplemented by electromagnetic or electrostatic processes; in many cases where these processes are not applicable, fire concentration may be adopted. The method aims to burn the zinc out of the ore and to collect it as a fume. In the Wetherill process (§139) of making zinc white from oxide ore, the purpose is to obtain an oxide which has a definite white color. In fire concentration the color of the oxide is of no importance, as the product either goes to the spelter furnace or forms an intermediary product which is treated by a separate process. The apparatus used are a grate with forced draft, a blast furnace, or a reverberatory furnace.

F. L. Bartlett¹ used at Cañon City, Colo., a form of Wetherill grate to treat sulphide zinc-lead ore with over 20 per cent Zn, burned off most of the lead and zinc as oxides which he collected as zinc-lead pigment in a baghouse, and then smelted the clinkered residue with ore containing under 20 per cent Zn in a low water-jacket furnace, forming waste slag, matte to be worked up, and fume to be collected with that from the grate.

Hall² at Florence, Colo., smelts mixed zinc-lead ores with 20 per cent Zn in a dust-fired reverberatory furnace, makes slags with 30 to 50 per cent SiO_2 , about 5 per cent matte, and fume which is collected in a baghouse. Fume is treated at Keokuk, Iowa, by leaching with sulphuric acid and electrodepositing the zinc, and disposing of the lead residue to lead plants.³

The practice of Great Falls of smelting the residues from zinc leaching vats for slag, matte and fume is discussed in §132.

The treatment of residue from zinc retorts on a grate for impure oxide is noted in §132.

Pape⁴ worked up zincky slags of the Lower Harz by crushing to 2 in., briquetting with coal and a binder, burning the briquettes on the water-cooled grate of a boiler using suction draft, collecting the dust in a chamber to be retreated, and the fume in a baghouse to be worked in a spelter furnace.

Clerc⁵ constructed a kiln similar to the Taylor gas producer in

¹ Bartlett, *Min. Ind.*, 1896, v, 619.

Hofman, "Lead," 1918, p. 128, with cross references.

² Hofman, "Lead," 1918, p. 135.

³ Not in operation.

⁴ Glückauf, 1910, XLVI, 237; *Eng. Min. J.*, 1910, LXXXIX, 819; *Tr. A. I. M. E.*, 1910, XLI, 642.

⁵ *Eng. Min. J.*, 1913, XCV, 225.

which cold-air blast enters beneath the grate, and air heated by an air jacket is blown into the gas (fume) chamber through tuyeres; additional air is admitted into the exit flue to ensure complete conversion of the remaining CO into CO₂. The charge is made up of oxide ore, or oxide and sulphide, mixed with coal; the addition of sulphide reduces the amount of coal required.

SMELTING IN RETORTS

72. Introduction.—The development of the reduction of calcined or roasted zinc ore by means of carbon in retorts of refractory clay, heated by solid, liquid or gaseous fuel, has given rise to different forms of furnaces which have become types and are classed as Belgian, Rhenish (Belgian-Silesian), Silesian, English, and Carinthian. With each method there has arisen a method of operating, so that it is convenient to discuss the subject under the five heads given. With all of them there have to be considered the behavior in reduction of the charge components, the requirement of the refractory clays and manufacture of refractory vessels, and the preparation of the charges. These three subjects are therefore taken up first as covering common ground.

73. Reduction and Effect of Charge Components.—The components to be considered are C, CO, S; and compounds of Zn, Cd; Fe and Mn; Ca, Mg and Ba; Pb; As and Sb; further SiO₂ and silicate, CaF₂; and reducing fuel.

1. *Reducing Agents.*—The leading reducing agents are C, CO, and to a certain extent S. The reducing effect of C begins at 400°C. and increases with the temperature; that of CO begins at 200°C., increases to about 1,000° and then falls off; that of S begins at about 500° and increases with the temperature.

2. *ZnO, ZnSO₄, ZnSiO₃, ZnAl₂O₄, ZnFe₂O₄, ZnS.*—The behavior of these compounds has been taken up in §§25, 27, 30, 33.

3. *CdO.*—The properties of this oxide are taken up in §151. They show that the behavior of Cd and Cd-compounds is very similar to that of Zn, but that the reactions take place at lower temperatures. The result is that in distilling Cd-bearing Zn ore, the CdO ought to be reduced before ZnO, and Cd-vapor condensed before Zn-vapor. At the beginning of the distillation some of the Cd will come over before the distillation of the Zn is well started, and will collect largely in the blue powder formed at first. The first blue powder forms in European plants the raw material for the

production of metallic cadmium (§156). The rest of the Cd will come over with the Zn and be found in the spelter.

4. Fe_2O_3 , $FeSiO_3$, MnO_2 , $MnSiO_3$, FeS , MnS .—The reduction by C¹ begins with Fe_2O_3 at 400°C., with Fe_3O_4 at 450°, with FeO at 450°, with MnO_2 at 260°, with Mn_3O_4 at 430°, and with MnO above 600°. The reduction by CO begins with Fe_2O_3 at 200°,² with Fe_3O_4 above 450°,³ with FeO at 700°;⁴ the reduction of FeO is never complete on account of the reversibility of the reaction. Silicates of Fe and Mn are brought to the state of $Fe(Mn)_2SiO_4$ which have formation temperatures of 1,270°C.⁵ and 1,327°C.;⁶ they form slags with other base oxides which have lower formation and melting temperatures than the pure silicates. They interfere with the reduction of ZnO and attack the retort material. FeS melting at 1,187°C.⁷ will tend to form matte which holds back ZnS and corrodes the retort; MnS is present in such small amounts that it has no effect.

5. $CaSO_4$, $MgSO_4$, $BaSO_4$.—The reduction of $CaSO_4$ ⁸ to CaS takes place without loss of S; with C it begins at 700°C. and is finished at 1,000°; with CO it begins also at 700°, but is finished at 900°. An interaction between CaS and $CaSO_4$ is possible in a neutral atmosphere but cannot take place in one that is reducing. Lepiarczyk⁹ states that in the reduction of $CaSO_4$ to CaS there is formed some CaO if there is present ZnO or Fe (Mn)O, and that there is a loss of S, viz., $3CaSO_4 + CaS = 4CaO + 4SO_2$; he holds that the reactions $CaS + ZnO = CaO + ZnS$ and $CaS + FeO = CaO + FeS$ occur, that $CaSO_4$ has a sulphurizing effect upon ZnO and FeO as shown by $CaSO_4 + Zn(Fe)O = Zn(Fe)SO_4 + CaO$ and $Zn(Fe)SO_4 + 4C = Zn(Fe)S + 4CO$, and advocates with calcareous ores the addition of Fe_2O_3 to the charge to fix the S and prevent it from combining with the Zn. The addition of Fe_2O_3 will hardly commend itself on account of the corrosive effect it has upon the retort. Prost¹⁰ has shown experimentally that the reaction $CaS +$

¹ Wright-Luff, *J. Chem. Soc.*, 1878, XXXIII, 1.

² Bell, "Principles of Manufacture of Iron and Steel," Rutledge, London, 1884, p. 191.

³ Wiborgh, *Stahl u. Eisen*, 1897, XVII, 804, 858.

⁴ Wiborgh, *ibid.*

⁵ Hofman, *Tr. A. I. M. E.*, 1889, XXIX, 700.

⁶ Doerinckel, *Metallurgie*, 1911, VIII, 201.

⁷ Friedrich, *Metallurgie*, 1907, IV, 479.

⁸ Hofman-Mostowitsch, *Tr. A. I. M. E.*, 1910, XLI, 763.

⁹ *Metallurgie*, 1909, VI, 409.

¹⁰ *Bull. Assoc. Belge. Chim.*, 1896, x, 246.

$\text{ZnO} = \text{CaO} + \text{ZnS}$ does not take place; he has also shown (*Rev. Un. Min.* 1914. VII. 85) that an elimination of sulphur in roasted blende, present as alkali-earth sulphate, takes place, especially during the first twelve hours.

The reducing temperature of MgSO_4 with C or CO is not known; there exist no experiments to show whether the behavior of MgSO_4 is similar to that of CaSO_4 .

Mostowitsch¹ has shown that the reduction of BaSO_4 to BaS by C begins at 600°C . and is complete at 800° ; the reduction by CO begins at 650° and is complete at $1,050^\circ$; and that BaS is stable at $1,000^\circ$, but gives off some S at $1,200^\circ$. Wells² gives additional information.

Both MgSO_4 and BaSO_4 are of very little importance as they are present in zinc ores only in small amounts.

6. PbO , PbSO_4 , PbS and PbSiO_x .—Of these, PbO , which melts at 883°C .³ begins to be reduced by C at 400° to 500°C .;⁴ reduction is decided at 600° and quick at 700° ; reduction by CO begins at 300° .⁵

It has always been assumed that PbSO_4 was reduced by C or CO to PbS ; Mostowitsch⁶ has shown that in addition to PbS there are formed small amounts of Pb and SO_2 owing to the action of the newly formed PbS upon PbSO_4 . Reduction by C begins at 550°C . and is finished at 700° ; with CO it begins at 600° and is active at 630° . PbSO_4 is decomposed by SiO_2 at $1,030^\circ\text{C}$.⁷

PbS ought not to be present in roasted ore; it melts at $1,120^\circ$.⁸

PbSiO_x shows melting temperatures varying from PbO (883°C .) to $\text{PbO}\cdot\text{SiO}_2$ (about 760°); PbO and SiO_2 begin to combine at 710° .⁹ The lead in excess to that required to form Pb_2SiO_4 is reduced by C; FeS throws down some Pb; in order to set free all the Pb, some base is required to take its place.

7. *Ag-Au*.—Zinc ores from the Rocky Mountain division are likely to contain *Ag-Au*. These metals remain in the residue,

¹ *Metallurgie*, 1909, VI, 450.

² *Bureau Mines Bull.* No. 113, 1917; *J. Ind. Eng. Chem.*, 1916, VIII, 770.

³ Mostowitsch, *Metallurgie*, 1907, IV, 647.

⁴ Doeltz-Graumann, *Metallurgie*, 1907, IV, 420.

⁵ Brislee, *J. Chem. Soc.*, 1908, XCIII, 154.

⁶ *Tr. A. I. M. E.*, 1916, LV, 741.

⁷ Friedrich, *Stahl u. Eisen*, 1911, XXXI, 2040.

⁸ Friedrich, *Metallurgie*, 1908, V, 23.

⁹ Hilpert, *Metallurgie*, 1908, V, 535.

being taken up by lead or matte. If any precious metal is found in the spelter, its presence is due to mechanical entrainment.

8. *As* and *Sb* are of little importance.

9. SiO_2 and silicates are present to varying degrees in all ore. They affect the fusibility of the charges according to the general laws governing the formation of slags.

10. *Fluorspar*.—The CaF_2 found in a number of zinc deposits has a harmful effect on the life of retorts. While its melting point is high, $1,378^\circ\text{C}$., it forms *e.g.*, with CaSiO_3 , melting at $1,501^\circ\text{C}$., an eutectic¹ with 38.2 per cent CaF_2 melting at $1,130^\circ$. In smelting lead or copper ores in blast or reverberatory furnaces, CaF_2 renders refractory charges fusible; this points to the idea that it forms, with other substances than CaSiO_3 , eutectics of low melting points.

11. *Reducing Fuel*.—This is taken up below.

74-75. **Composition of Charge.**²—The charge are made up of a mixture of calcined and roasted zinc ore and about 50 per cent reducing fuel; usually there is added some zinc oxide formed in the distillation which has to be re-treated. As regards ore there have to be considered a number of points. The zinc-content has to be high. With the Belgian circular retort, 10 in. in diameter, the lowest permissible Zn-content is 35 to 40 per cent; with the Silesian muffle, $5\frac{1}{2}$ in. wide by $26\frac{1}{2}$ in. high, carbonate ores with as little as 8 to 9 per cent Zn are added to the charges, and ores with 20 to 30 per cent Zn are not uncommon.³ At La Salle, with Belgian retorts⁴ Missouri and Wisconsin ores were mixed to contain Zn 66 – 70, SiO_2 7-12, Fe 1.5-2, CaSO_4 1.75 per cent; an average analysis gave ZnO 86.95 (Zn 69.82), CdO 0.36, CuO 0.08, PbO 0.37, Fe_2O_3 1.28, Al_2O_3 2.22, CaO 0.80, MgO 0.07, SiO_2 7.00, S 1.19 per cent.

The reducibility and with it porosity and size of particles are of importance. Zinc silicate is most difficult of reduction, then follow roasted blende, calcined carbonate, blue powder and zinc oxide from the furnaces which have to be re-treated. An ore that resists reduction is usually dense, hence CO has little effect upon it; this necessitates an intimate contact with C, which requires fine grinding, in addition the temperature has to be high. Usually ores difficult of reduction are mixed with ores that yield their zinc more

¹ Karandief, *Zt. Anorg. Chem.*, 1910, LXVIII, 188.

² Juretzka, *Metallurgie*, 1907, IV, 84; 1911, VIII, 1; *Rev. Mét. Extr.*, 1911, VIII, 1.

³ Steger, V., "Verdichtung der Metaldämpfe in Zinkhütten," Stuttgart, Enke, 1896, p. 48.

⁴ Mühlhaeuser, *Metall u. Erz.*, 1918, XV, 123.

readily, especially if the temperature of the furnace is uniform. If this is not the case, difficult ores are placed in the hotter and the easy ores in the cooler parts; another means of counter-acting this inequality in reduction is to have retorts of different diameters, the difficult ores will go into retorts of small and easy ores into vessels of large diameter. It is, however, common practice to add some easy ore to a difficult charge in order that the zinc vapor from the easy ore may fill the retort as soon as possible and expel the harmful gases and vapors set free at the beginning of the process. Mühlhaeuser¹ found that the pressure of gas vapor in a retort did not materially influence the yield of spelter.

The gangue in the ore is either acid or basic. It is advisable to treat these two classes of ores separately in order to prevent slagging. As the charge during distillation loses about 50 per cent in weight and shrinks to a considerable extent, the gangue particles held apart at first by the reducing fuel come together more closely and combine, if the chemical conditions are favorable. If siliceous and basic ores have to be treated together, it is necessary to mix them in such proportions that only slags of high formation temperatures can form, that is slags running high in SiO_2 or CaO or Al_2O_3 . The most harmful bases are FeO , MnO , PbO , and alkalis. An average sample of slag formed at La Salle gave Mühlhaeuser² SiO_2 65.12, Al_2O_3 16.86, FeO 7.92, CaO 7.02, MgO 0.65, K_2O 0.29, Na_2O 0.42, CuO 0.10, ZnO 2.64, S 0.98 per cent. The ores from the Central States run low in iron, about 2 to 3 per cent. A furnace charged with such ore can be run at a high temperature without corrosion of retorts. Western ores are likely to be rich in iron, 10 to 12 per cent; an ore from Leadville, Colo.,³ with Zn 40, Fe 17, Pb 4 per cent, which after roasting assayed Fe 20 per cent, has been smelted alone but, of course, gave a low yield in zinc, and made much blue powder. The bad effect of Fe_xO_y is usually counteracted in part by bringing the charge quickly to a high temperature in order to reduce Fe_xO_y to Fe, holding it there for 6 hr. or longer, and drawing as much metal as possible, then lowering the temperature to hinder slag-formation, and holding it at the low temperature to the end of the 24-hr. period of distillation.

Reduction of Fe_xO_y by heating the charge in a closed vessel

¹ *Metall u. Erz*, 1919, XVI, 363.

² *Metall u. Erz*, 1918, XV, 304.

³ Ingalls, *Min. Ind.*, 1907, XVI, 928.

previous to smelting is carried out by Johnson¹ in his electric smelting process. A different method of procedure is used by De Saulles² who on the last hearth of a Hegeler roasting furnace adds 5 per cent coal to the charge that is nearly finished, and maintains a temperature of 800° but does not allow it to exceed 1,000°C. Beside reducing Fe_xO_y to Fe, he aims to reduce MSO_4 . This process, in operation at the works of the United States Zinc Co., Blende, Colo., has caused the life of retorts to be lengthened by 6 days, and the yield of zinc raised from 80 to 85 and 86 per cent. A similar idea has been patented by A. Roitzheim.³

The lead-content is harmful, as PbO is a powerful base, but most of it is reduced to metal before ZnO, hence the slagging effect is not as powerful as might be expected. A content of even 10 per cent does little harm provided the temperature in the furnace is not kept too high, say below 1,300°C.

Alkalies are harmful in that they slag almost anything at low temperatures, and the slags are pasty even at high temperatures and form a corrosive glass.

Alumina or aluminum silicate which is difficult of fusion, makes ferro-calcic silicates glassy.

Ore mixtures have to be calculated in a manner similar to the one used in making up lead or copper blast-furnace charges in order to permit a study of the probable effects of the components.⁴

Salt⁵ is sometimes added to the ore to the extent of 0.2 per cent with the object of reducing the amount of zinc oxide formed, of keeping bright the zinc in the condenser, and of having a flame issuing from the condenser colored yellow to near the end of the distillation. The use of salt is not general. Its action is not explained. Salt melts at about 800°C. and fumes when molten. The fume may expel air and it does color the flame. It may also react with ZnSO_4 and form ZnCl_2 , but ZnCl_2 added to the charge has no effect; some metallurgists hold that a double salt of ZnCl_2 and NaCl acts as a solvent for ZnO; drops of ZnCl_2 have been found adhering to the wall of the condenser. Recent experiments by Ravner (*Chem. Met. Eng.* 1921, XXIV, 932) in recovering metallic zinc from fluedust by heating with ZnCl_2 and NaCl furnish a clue.

¹ *Tr. Can. Min. Inst.*, 1914, XVII, 109.

² *Eng. Min. J.*, 1916, CII, 91.

³ U. S. Patent No. 1,100,490, June 16, 1914.

⁴ Juretzka, *Metallurgie*, 1907, IV, 84.

Hofman, "Lead," 1918, pp. 331-339; "Copper," 1918, pp. 185, 202.

⁵ Kiessling, *Berg. Hüttenm. Z.*, 1903, LXII, 613.

It has been found that 2 per cent NaCO_3 acts in a manner similar to 0.5 per cent NaCl .

76. Reducing Fuel.—The reducing fuel added to the charge ranges from 40 per cent with calcined carbonate ore to 60 per cent with roasted blende; at Carney, Kan., it amounted to 60 and 75 per cent of the weight of the ore. This is a great excess over the amount necessary for reduction proper; it is required to ensure reduction of CO_2 formed, to keep the charge coarse and thus prevent it from sintering.

The fuel ordinarily used is a mixture of clean non-caking or only slightly caking bituminous coal slack, low in V. H-C which it does not give up readily, coke-breeze, and cinder. The best reducing fuel is Pennsylvania anthracite buckwheat No. 2, which passes through a screen $1\frac{3}{8}$ to $\frac{3}{8}$ in. and weighs $50\frac{3}{4}$ lb. per cubic foot; an older analysis¹ shows H_2O at 225°F . 0.10, V. H-C 5.25, ash 15.50, fixed C 75.5 per cent; sp. gr. 1.664. The anthracite used at La Salle gave Mühlhaeuser² H_2O 1.60, V. H-C 7.89, F.C. 80.12, ash 10.39. The ultimate analysis of ash-free coal gave C 82.50, H 3.87, S 0.97, N 0.63 per cent. Anthracite is used largely east of the Mississippi River. The reducing fuel must be clean, *i.e.*, free from slate, pyrite and other harmful substances. It is frequently washed to meet these requirements.

Bituminous coal evolves in the retort heavy V. H-C which being dissociated in part deposit finely divided C which is a powerful reducing agent. If used alone, it would make too much gas which would dilute the zinc vapor and cause the formation of an excess of blue powder; in addition, the expulsion of V. H-C in a retort is an expensive operation.

Coke, which contains about 2 per cent V. H-C, does not dilute the zinc vapor. It is not desirable to use it alone, as it requires a high temperature to be effective, does not deposit any finely divided C, and does not furnish enough CO to give the necessary pressure in the retort for forcing out Zn-vapor and preventing air from entering through the mouth of the condenser or CO_2 through the sides. The proportions of coal and coke used vary greatly; the coke does not exceed 25 per cent of the total fuel used, a more common proportion is half this amount.

Cinder is partly degasified coal, partly burned coal from direct-fired distilling furnaces or from gas producers.

¹ Coxe, *Tr. A. I. M. E.*, 1893, XXII, 603.

² *Metall u. Erz*, 1918, XV, 163.

77. Mixing of Charge.—Ore and reducing fuel are crushed separately; roasted blende to pass a 2-mm. hole or 60-mesh screen, calcined carbonate ore and reducing fuel to pass 5- or 6-mm. hole, or 3- or 4-mesh screen. Rolls commonly serve for this purpose. The mixing of the ground materials varies with the size of the plant. In all cases some water is added, as it assists intimate mixing, counteracts dusting, and helps packing when charging the mixture into the retort. In small plants the lay-down or pit-system is still in use, *i.e.*, the ore and fuel are spread in one or two pits in superposed layers. When a pit is filled, its content is shoveled direct into a car or it is first passed through a conveyor to insure

good mixing which delivers into the boot of a bucket elevator discharging into a car. The cost of mixing with the pit-system, treating from 70 to 100 tons per day is from \$0.204 to \$0.176 per ton of ore.¹ In large plants manual labor is done away with as much as possible.

A Vapart mill² shown in vertical section in Fig. 83, consists of a vertical stationary cast-iron cylinder with three corrugated chilled-iron rings, *a*, and hopper-shaped chutes, *e*; and of a central revolving shaft, *b*, with three horizontal discs having radial fins on their surfaces. The ore mixture fed

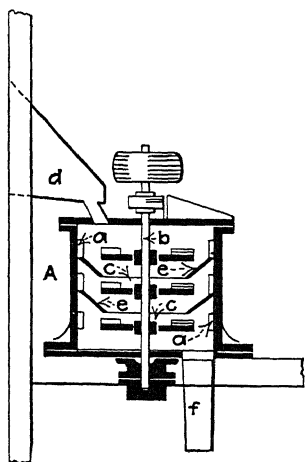


FIG. 83.—Vapart mill.

through chute *d* is thrown by centrifugal force against ring *a*, is somewhat broken, drops, and is delivered by chute *e* to the center of the second disc, and so on until it arrives at the bottom to be discharged into a conveyor car. A three-disc machine has an inner diameter 4 ft. 1¼ in., is 3 ft. 7⅞ in. high, has a pulley 19.7 in. in diameter and 9.4 in. in width, makes 600 to 900 r.p.m., requires from 8 to 12 hp., and handles per hour from 7½ to 10.0 tons ground mixture. The amount treated is smaller if some grinding has to be done in the mill. The apparatus was in operation with the Bartlesville Zinc Co.³

¹ Johnson, *Met. & Chem. Eng.*, 1917, XVI, 377.

² Cordier, *Bull. Ind. Min.*, 1880, IX, 391.

Anon., *Berg. Hüttenm. Zt.*, 1883, XLII, 68.

Kahr, *Metall u. Erz*, 1913, X, 899.

³ Ingalls, *Min. Ind.*, 1907, XVI, 926.

The continuous feeding of ore and coal into the Vapart mill is likely to result in a mixture that is not uniform, hence apparatus which receive charges and work intermittently are preferred. The Ransome mixer¹ shown in perspective in Fig. 84, is of this character. It is a motor-driven horizontal drum, 60 in. in diameter and 46 in. long, made of $\frac{3}{16}$ -in. steel plate which has wing plates as stirrers.

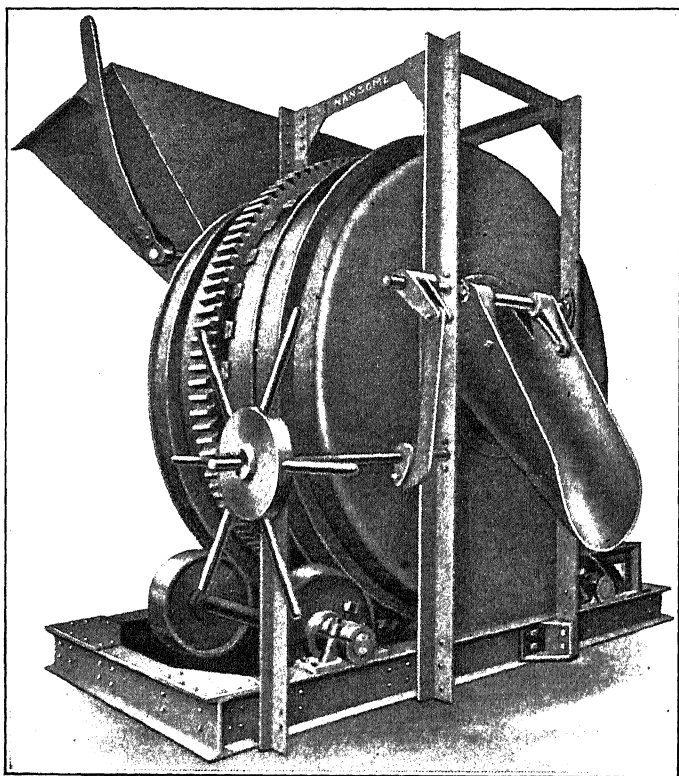


FIG. 84.—Ransome mixer.

At one end is a stationary pyramidal, steel plate No. 10 feed hopper, 78 by 42 in. at the top, which slopes at an angle of 45 deg. and delivers the components through a receiving opening 21 in. in diameter; at the other a tilting trough-shaped steel ($\frac{3}{16}$ in.) discharge-hopper, 20 in. wide and 48 in. long, which receives the mixture from an opening 21 in. in diameter. The floor space needed is 156 by 138 $\frac{1}{4}$ in.; the steel frame, of 10-in. channels, is 58 in. long, 43 in. wide, and

¹ Ransome Concrete Machinery Co., Dunellen, N. J.

156 in. high. The mixer requires a 15-hp. motor which is direct connected, makes 18 r.p.m. and receives a charge of 3,000 lb. which it treats in 1 to 2 min. and discharges in 16 sec. At Bartlesville, Okla., it handles in 8 hr. 122 tons ore. The cost of mixing from 110 to 125 tons per day is about \$0.14 per ton.¹

Other mixers are those of Raps and of Dor-Delattre² which are common in Europe.

As the mixture of ore and fuel is voluminous, it has been suggested to reduce the volume by briquetting. Thus Binon and Grandfils³ at Bleyberg, Belgium, mixed zinc ore with hot tar, compressed the mixture into cylinders of the diameter of the retort; they thus increased the amount charged into the retort by 50 per cent, diminished the reducing fuel by 10 to 15 per cent, and finished the heavier charges in the usual 24 hr. The method has not found general application although it has been tried by others; e.g., Kirkpatrick, Picard and Sulman⁴ who briquetted roasted ore with 20 per cent crushed coking coal and pitch, and charged the briquettes into retorts.

Recently briquetting has been recommended by Johnson.⁵ He ground ore and coal through an 80-mesh screen, added broom straw to make the charge coarse and conductive and to provide a free path for the passage of the gases, used from 10 to 12 per cent kerosene-acid sludge (obtained from refining a paraffine-base oil) as binder. The mixture was passed through an auger machine which furnished extrusions $\frac{1}{2}$ in. in diameter; these broke into pieces and dropped on a floor, were dried, and then charged in the usual way. By grinding coal and ore to 80-mesh he obtained an intimate contact of components; this enabled him to diminish the amount of reducing fuel from 60 to 30 per cent; further, the reduction in fuel permitted increasing the weight of the charge of a retort which was raised from 67 to 100 lb.

Between the extremes of Binon-Grandfils and Johnson lies the practice of compressing a usual charge, moistened with about 3 per cent water, in an apparatus similar to the Chisholm, Boyd, and White mineral press⁶ with the aim of expelling the air by compacting

¹ Johnson, *Met. & Chem. Eng.*, 1917, XVI, 377.

² Prost, *op. cit.*, pp. 55 and 57, or Liebig, *op. cit.*, pp. 375, 379.

³ *Rev. Un. Min.*, 1879, VI, 729; 1882, X, 61; *Berg. Hüttenm. Z.*, 1881, XL, 27; 1883, XLII, 198, 211; *Eng. Min. J.*, 1882, XXXIII, 4.

⁴ *Tr. Inst. Min. Met.*, 1901-02, X, 430.

⁵ *Tr. A. I. M. E.*, 1918, LIX, 156; *Eng. Min. J.*, 1918, CV, 370.

⁶ Hofman, "Lead," 1918, p. 462.

the components. The briquettes have so little strength that they crumble more or less when thrown into a car; they are introduced into the retort as is a loose charge, the weight of the charge in a retort, however, has been increased by 15 per cent.

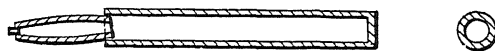


FIG. 85.—Belgian retort.



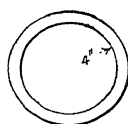
FIG. 86.—Rhenish retort.



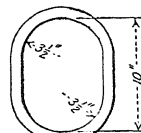
FIG. 87.—Silesian muffle.

78. Retorts and Muffles, Preparation of Mixture.¹—Leaving out of consideration the crucible of the former English method of working, the closed clay vessels in use at present are the cylindrical or elliptical Belgian retort, the oval Rhenish retort, and the Silesian muffle. Longitudinal and transverse sections of the three types with condensers attached are given in Figs. 85, 86 and 87 by Steger.²

The Belgian retort, Fig. 85, is a cylindrical or elliptical vessel supported at the ends and slightly inclined with the mouth pointing downward (Fig. 114). The external length of the cylindrical vessel ranges from 36 to 60 in., the inner diameter from 4 to 8 in., the thickness of side wall is 1 to 1½ in., and of bottom from ½ to 2 in.; the second figures correspond to the dimensions common today. A baked modern retort weighs about 135 lb. In



Area 50 Sq. in.



Area 60 Sq. in.

FIG. 88.—Cylindrical Belgian retort.

FIG. 89.—Oval Belgian retort.

¹ Juretzka, *Metall u. Erz*, 1913, x, 78; *Feuerungstechnik*, 1915, III, 106.

Mühlhaeuser, *Zt. angew. Chem.*, 1903, 148, 222, 273, 321, 391, 738, 761, 1,055, 1,107, 1,224.

Johnson, *Met. & Chem. Eng.*, 1916, XVII, 475.

Babcock, *Jl. Am. Cer. Soc.*, 1919, II, 81.

² "Verdichtung der Metaldämpfe in Zinkhütten," Enke, Stuttgart, 1896, p. 76.

many instances the cylindrical cross-section has been replaced by one that is elliptical because a retort is stronger and therefore can be made longer or receive a thinner wall; it can also have a larger cross-section area which means that it can receive a heavier charge. Figures 88 and 89 show cross-sections of the two forms.

Table 25 gives the dimensions of auger and hydraulic retorts of five different plants measured by Johnson.¹

TABLE 25.—RETORT DIMENSIONS

	Diameter, inches	Length, inches	Wall, inches	Butt, inches	Kind	Cubic feet capacity
No. 1.....	$8\frac{1}{8}$	45.3	$1\frac{3}{16}$	$2\frac{1}{2}$	Auger	1.360
No. 2.....	$8\frac{1}{2}$	48.0	$1\frac{3}{16}$	$2\frac{1}{2}$	Auger	1.576
No. 3.....	$7\frac{3}{4}$	49.4	$1\frac{1}{16}$	$1\frac{1}{2}$	Hydraulic	1.349
No. 4.....	$8\frac{3}{16}$	50.5	$1\frac{1}{16}$	$1\frac{1}{2}$	Hydraulic	1.539
No. 5.....	$8\frac{3}{8}$	$49\frac{1}{4}$	$1\frac{1}{16}$	$1\frac{1}{2}$	Hydraulic	1.656
Average.....	$8\frac{3}{16}+$	$48\frac{1}{2}$	...	..		1.496

The Rhenish retort, Fig. 86, supported in the same manner as the Belgian, is always oval; a typical form is the one shown in Fig. 90. The length is 49 to 63 in., the major axis 10 to 13 in., the minor 6 to 7 in., the thickness of side wall 1 to 1.20 in., that of bottom 1.2 to 1.6 in., the weight 160 lb.

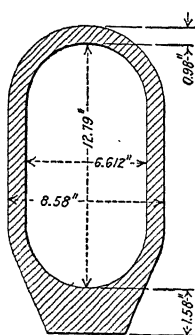


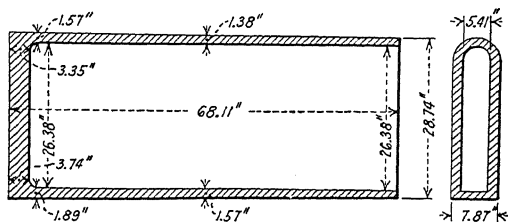
FIG. 90.—Rhenish retort.

The Silesian muffle, which has a flat bottom, straight sides, and an arched roof, rests with its entire bottom on a support and is somewhat inclined from back to front. A longitudinal and transverse section is shown in Figs. 91 and 92. The length of the muffle is 63 to 68 in., the width 6 to 8 in., the height 21 to 26 in.; the thickness of side walls increases from front to back, being 1 to $1\frac{1}{2}$ in., the bottom is 2 in. thick, and the back 3 in. at the top and 3.5 in. at the bottom. The weight air dried is about 200 lb. The diversity in thickness of walls has made it difficult to employ machinery in molding.

The requirements which the raw material and the method of

¹ *Met. & Chem. Eng.*, 1917, XVI, 477.

manufacturing of a retort have to fulfill are exacting. With the Belgian and the Rhenish retorts the raw material must be very refractory, *i.e.*, it ought not to melt at Seger cone 32 ($1,710^{\circ}\text{C.}$), nor soften at Seger cone 10 to 14 ($1,300^{\circ}$ to $1,410^{\circ}\text{C.}$) when the retort holds its charge about 130 lb. These figures represent European standards, where the temperatures maintained are higher than in the United States; here the refractory standard is Seger cone 28 or $1,630^{\circ}\text{C.}$ With the Silesian retort, supported on the entire bottom, the need of remaining rigid at cone 10 to 14 is not so essential. With the three types, the walls ought to be thin, in order that the heat of the furnace may penetrate into the charge. The only refractory material which is used is fireclay, and this in spite of its



FIGS. 91 and 92.—Silesian muffle.

being a bad conductor of heat, of having a tendency to crack when subjected to change of temperatures, and of resisting slagging to an unsatisfactory degree. Clay consists of the refractory constituents kaolinite and quartz, and of the non-refractory, which are more or less decomposed feldspathic minerals and act as fluxes. The dividing line between a refractory and a non-refractory clay lies at Seger cone 26 ($1,580^{\circ}\text{C.}$); the former will not, the latter will melt at this temperature. A clay to be used in making retorts must not melt at Seger cone 32 ($1,710^{\circ}\text{C.}$) according to European standards, or at cone 28 ($1,630^{\circ}\text{C.}$) in the United States, *i.e.*, it must be a high-grade refractory material. The refractory constituents are kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{H}_2\text{O}$, with SiO_2 46.3, Al_2O_3 39.8, H_2O 13.9 per cent), melting at Seger cone 35 ($1,770^{\circ}\text{C.}$), and quartzite (SiO_2), melting between Seger cones 27 and 28 ($1,625^{\circ}\text{C.}$). Al_2O_3 melts at $2,010^{\circ}\text{C.}$;¹ it forms with SiO_2 the compound $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (sillimanite) with Al_2O_3 62.85 and SiO_2 37.15 per cent which melts at $1,811^{\circ}\text{C.}$ ² and this forms with SiO_2 an eutectic with Al_2O_3 13

¹ Kanolt, *Techn. Paper* 10, U. S. Bureau of Standards, 1912.

² Wright, *Am. J. Sc.*, 1915, XXXIX, 1.

and SiO_2 87 per cent, melting at $1,610^\circ\text{C}$. Kaolinite can therefore have a considerable admixture of silica and still be sufficiently refractory to serve as raw material. The principal non-refractory components of a clay are MgO , CaO , FeO , Na_2O , K_2O . With a water-free clay their total ought to be less than 6 per cent if the clay is to stand a temperature of Seger cone 26.

Beside the refractoriness there have to be considered plasticity and shrinkage. Residual clays (kaolin, rock or flint-clays) have as a rule high melting points and are non-plastic; sedimentary or fat clays generally have lower melting points than those that are lean, but are more or less plastic and have a large shrinkage, hence lean and fat clays are combined in such proportions that the mixture shall shrink evenly and become dense at a low temperature. Cal-cined clay (grog) is non-plastic, nor does it shrink. Quartzite expands upon heating. Coke may shrink a little upon heating, if it retains more than the usual amount of V. H-C, but practically it does not. The addition of coke to a clay mixture is said to diminish the formation of spinel.¹ The proportions to be used vary greatly with the character of the raw materials. In a general way it may be said that a mixture of 60 to 70 parts non-plastic and 30 to 40 plastic material fulfills the requirements of a retort clay. The plastic clay is supposed to envelop the particles of non-plastic clay and to bind these into a compact mass; the grog to absorb water in pugging and to give it off gradually to the bonding plastic clay, thus making the rate of evaporation uniform during drying. Table 26 gives examples of retort mixtures.

A few analyses of American fireclays used in making retorts are given in Table 27; of other clays used in the Central Western States are given by Johnson.²

Analysis of clays used in Silesia, Rhenish Prussia and Belgium have been assembled by Steger.³

While chemical analyses show in a general way whether a clay is refractory or not, tests for refractoriness,⁴ shrinkage, and general behavior of clay and mixtures have to be made to give an answer which approximately corresponds to the behavior in the furnace. Thus at Palmerton, Pa.,⁵ the clay or clay mixture is tamped into a

¹ Proske, *Metall u. Erz*, 1914, XI, 333, 377, 412, 553.

² *Met. & Chem. Eng.*, 1917, XVI, 476.

³ *Zt. B. H. u. S. W. i. P.*, 1896, XLIV, 1.

⁴ Hofman, *Tr. A. I. M. E.*, 1895, XXV, 3.

⁵ Fiske, *Tr. A. I. M. E.*, 1917, LVII, 868.

TABLE 26.—RETORT MIXTURES, VOLUMES

Raw clay	Burnt clay	Old retorts	Coke	Quartz	
40	50	..	10	..	Z. B. H. & S. W. i. P., 1896, XLIV, 1.
36	54	..	10	..	
30	10	50	10	..	
35	34	26	2	3	
30	27	15	18	1	Massart, <i>Rev. Un. Min.</i> , 1871, XXIX, 322.
45	15	40	..	..	Thum, <i>Berg. Hüttenm. Z.</i> , 1859, XVIII, 406.
34	30	22	..	14	
34	52	7	7	..	Fiske, <i>Tr. A. I. M. E.</i> , 1917, LVII, 877, Palmerton, Pa.
46	48	..	6	..	
40	50	..	10	..	Babcock, <i>J. Am. Ceram. Soc.</i> , 1919, II, 90.
36	54	..	10	..	

TABLE 27.—ANALYSES OF AMERICAN FIRECLAYS USED IN RETORTS

	Golden, Colo.	St. Louis, Mo.	Cheltenham, Mo.	St. Louis, Mo.	Mt. Savage, Md.	Sayreville, N. J.	Woodbridge, N. J.	South Amboy, N. J.	Clearfield, Pa.
Al ₂ O ₃	31.72	23.26	31.53	35.02	38.14	38.66	35.90	39.24	39.58
SiO ₂	51.21	59.68	50.80	50.02	47.83	44.20	46.10	43.41	45.20
MgO.....	0.23	0.42		0.46	0.17				0.24
CaO.....	0.36	0.65		0.70	tr.			0.20	0.33
Fe ₂ O ₃	0.75	3.24	1.92	2.76	1.31	0.74	1.10	0.46	1.31
K ₂ O.....	0.48	0.54	0.40	0.06	0.49	0.28	0.28	0.89	0.34
Na ₂ O.....	0.45	0.79		0.17	0.52	0.18	0.16		
TiO ₂	x	x	1.50		5.90	1.20	1.30	1.60	
H ₂ O.....	14.13	12.94	13.80	12.51	13.80	14.55	14.30	14.90	13.18
Total.....	98.50	98.48	99.95	101.70	100.98	99.81	99.94	100.70	100.18
Seeger Cone.....	$\frac{33}{31}$	$\frac{33}{32}$			$\frac{34}{35}$	35			$\frac{33}{34}$
Reference.....	1	1	2	5	1	1	2	3	4

x Included in SiO₂.

1. Hofman, *Tr. A. I. M. E.*, 1895, XXV, 14, 16.
2. Moxham, *Eng. & Min. J.*, 1893, LVI, 544.
3. Ries, *Min. Ind.*, 1893, II, 209.
4. J. Sp. McDowell, Private Notes.
5. Mühlhaeuser, *Zt. angew. Chem.*, 1903, XVI, 149.

mold such as is used for cement testing, air dried for 1 day, dried for 1 day at 110°C., and then burned at 1,200° to 1,300°C. for 24 hr. The data obtained from air, steam and fire shrinkage, and for tensile strength are compared with the standard clays and mixes.

In a furnace a retort has to resist deformation, fusion, corrosion, breaking by impact, sudden change of temperature, and permeation by gases and vapors; in one word it must be able to work many charges and furnish a high yield of zinc.

The preparation of the mixture embodies the following steps. The components, raw clay, previously dried if necessary, and burnt clay, perhaps pulverized quartzite and coke, are bedded, passed through a crusher with discharge set at $\frac{1}{2}$ in.; the coarsely broken mixture is reduced in size by edge rollers (dry-pans) or ordinary rolls or disintegrators and passed through a 6-mesh screen with No. 16 wire. Clay and grog are often crushed separately, the former through a 6-, the latter through an 8-mesh screen. If crushed too fine, the retort is likely to crack or soften and bend in the fire, if too coarse it will be too porous. The permeability¹ of a retort is governed by the internal pressure; with a high pressure less gas flows out of the condenser with a lower N-content than with a low pressure.

Screen analyses by Johnson² are given in Table 28.

TABLE 28.—SCREEN TESTS ON CRUSHED RETORT MIXTURES

Mesh	No. 1, 6-mesh No. 16 wire, per cent	No. 2, 6-mesh No. 16 wire, per cent	No. 3, piano wire, per cent
On 8.....	3.00		
On 10.....		16.00	30.8
On 20.....	55.02	25.90	28.5
On 30.....		26.70	13.5
On 40.....	21.11	7.30	6.5
	79.13	75.90	79.3
On 60.....	8.81	6.60	4.5
On 80.....	2.51	5.90	6.8
On 100.....	1.51	2.10	3.0
Through 100.....	8.04	9.60	6.4
	20.87	25.10	20.7

¹ Mühlhaeuser, *Metall u. Erz*, 1919, XVI, 323; *Eng. Min. J.*, 1919, CVIII, 729.

² *Met. & Chem. Eng.*, 1917, XVI, 476.

The finished mixture is now fed with water into a horizontal pug mill; from 16 to 20 per cent water are required if the retort is to be molded by hand or an auger-shaped machine, from 10 to 14 per cent if made with a hydraulic press. The tempered clay is piled in the form of balls or cylinders in heaps or pits, covered with sacking to counteract evaporation, allowed to weather for from 3 to 8 weeks in order to increase plasticity, and then worked for a second time before molding. At Palmerton, Pa., the rotten cylinders are worked in a vertical pug mill; the issuing cylinder, 14 in. in diameter, is cut into lengths of 15 to 17 in. which will weigh 200 lb. The increase in plasticity is ascribed to water soaking, oxidation of organic matter, to the production of colloids by hydrolysis, and to bacterial action. The two pits at Palmerton, Pa.,¹ hold 1,700,000 and 2,500,000 lb. mix; steam is introduced when the weather is too dry or too cold. The length of time given to rotting may have a weakening influence upon tensile strength. Thus Fiske, with St. Louis clay dried at 110°C. shows that 24 hr. rotting gives the strength of 67.5 lb.; 1 week, 83 lb.; 2 weeks, 93 lb.; 3 weeks, 67 lb.; and 4 weeks, 39 lb. The clay after 2 weeks rotting shows the greatest strength.

79. Molding of Retorts and Muffles, General.—Cylindrical and oval retorts used to be molded by hand, at present this is done by machinery; muffles on the other hand which have increasing thickness from front to back are molded by hand today.

80. Molding Retorts by Hand.—This method, while obsolete, has many points of interest.² A mold consists of three detached sheet-iron cylinders about 14 in. high; a cylinder is made up of two trough-shaped pieces joined by hinges and closed either by hooks and eyes or by loops and wedges. The lowest mold is placed upright on the floor; a wall of tempered mixture is dropped in, and tamped with a cylindrical rammer of the same diameter as the inner diameter of the retort. There is formed a cylindrical cup. The retort is built up on the rim by winding in form of a coil a rope of clay; every coil is tamped down and the cylindrical form preserved by removing irregularities and by patting with a semi-cylindrical wooden tool. While winding, the adjoining surfaces of the rope are roughened that they may adhere firmly. When the bottom cylinder is nearly filled, the central cylinder is placed on top, fastened by ring and wedges, and winding continued; the operation is repeated with the top cylinder. A man makes from 18 to 20 retorts in 10 hr.

¹ Fiske, *loc. cit.*

² Thum, *Berg. Hüttenm. Z.*, 1859, XVIII, 406, Plate XVI.

The retorts remain 48 hr. in the molds that they may come to a set; they are removed and given the mark of the maker and the date; are air-dried for from 1 to 3 weeks, when they shrink from 5 to 6 per cent; transferred to the first drying chamber in which a temperature of 30°C. is maintained, and kept there 3 weeks; then to a second drying chamber which is held at 70°C. where they remain 3 weeks or longer, until they go to the baking oven. Hand molded retorts used to be painted on the outside with a glaze made up of low-grade clay, sand, salt, and soda. With machine made retorts this has proved to be superfluous, except when coke is present in the molding mixture; then a glaze is applied in many cases, but not always, showing diversities of opinions or experiences.

81. Molding Retorts by Machinery.¹—The earliest case of mechanical manufacture of retorts is the one with the Dorr machine.

1. *Dorr boring machine*, patented in 1853, was introduced at Angleur and St. Leonard, Belgium.² A cylindrical cast-iron mold, divided longitudinally into two parts and clamped, is lined with a wet canvas bag; balls of clay mixture are rammed into it by a gravity or steam hammer; the filled mold is placed under a vertical boring machine, and the cylinder reamed out. When the retort has come to a set, the mold is removed, the retort placed in the dry house, the canvas bag stripped, and the surface of the retort smoothed with a wooden tool. In 10 hr. seven men make 140 retorts with 12 molds.

2. *Auger Machine*.³—This method, which originated in the United States and is still largely used in Kansas, Missouri and Oklahoma, has been replaced to some extent by the Dor hydraulic press, at least in large smelteries.

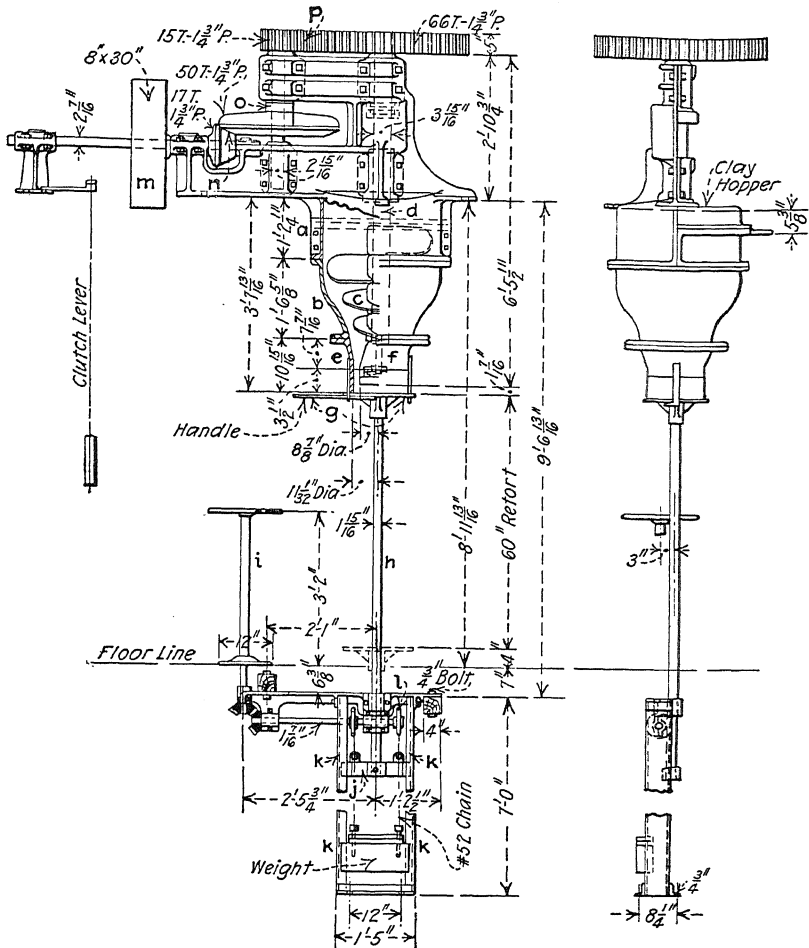
The auger machine, made by the United Iron Works Co., of Iola, Kan., is shown in Fig. 93, in part vertical section and side view, and 94, end view. Its leading element is a vertical casting with three divisions, an upper cylinder *a* to receive balls of pugged clay, a middle hopper *b* in which blades *c* on a revolving shaft *d* pug and press downward the clay, and a bottom bell *e* with central core *f* between which the clay is forced out forming a cylindrical pipe. Beneath the casting is a pipe-table *g* attached to the head of a counterbalanced shaft *h* controlled by a hand wheel *i*. The emerging

¹ Hiard, *Rev. Un. Min.*, 1881, IX, 184; *Berg. Hüttenm. Z.*, 1882, XLI, 102, 110; *Eng. Min. J.*, 1882, XXXIV, 195.

² Ill. in Lodin, "Metallurgie du Zinc," p. 632.

³ Mühlhaeuser, *Zt. angew. Chem.*, 1903, 274.

clay pipe is received on the table and presses downward the latter as it issues from the bell. The lower end of the shaft has a cross-head j gliding in guides k which steadies the motion. In passing downward, the crosshead raises, by means of two attached No.



FIGS. 93 and 94.—Auger retort machine.

52 chains, the counterweight of 80 lb. which glides in the same guides *k* as the crosshead of the shaft. Auxiliary weights of 6 lb. serve to readjust the counterbalance. When a pipe has attained the desired length, the machine is stopped, and the pipe cut off at the top by

means of a wire. The weight now returns to its original position and raises the shaft with its table to the mouth of the cylinder; the speed of the motion is regulated by hand wheel *i* through bevel gears and horizontal shaft which carries sheaves *l* of the chains. The machine, intended for a retort 60 in. long and $8\frac{7}{8}$ in. in diameter when moist, receives its power through a pulley *m*, 8 by 30 in., which is transmitted through bevel gears *n* to vertical shaft *o* and then through pinion and spur wheels *p* to the main shaft *d* provided with pugging blades *c* set at the proper angle.

The pipe when cut off is enclosed by two semicircular pieces of wood which are fastened by iron rings to form a cylindrical mold. The mold with its pipe is removed to one side and the bottom of the retort put in. For this purpose the mold is placed in a horizontal position, the bottom and adjoining side of the pipe are roughened, the mold is righted and a ball of pugged clay thrown in and rammed down firmly with a rammer having a head corresponding to the diameter of the retort.

At some works the cast-iron bell *b* has a hinged gate swinging in a horizontal plane which closes the discharge, and turns inward the bottom of the clay pipe. When this is accomplished, the machine is stopped, the gate opened and the machine started again. The pipe now descends in the usual way. In Fig. 93 the bottom plate *g* has a handle *q* which is held in hooks attached to bell *e*, and serves the same purpose as the hinged gate. In putting in the bottom, a conical lump of clay is inserted from below, joined to the pipe by rubbing with the ball of the hand, and the excess clay removed. The mold is now righted and the protruding part of the conical lump of clay rammed down thoroughly with four or five blows. A retort remains in a mold for 48 hr., or the mold is replaced by three or more wooden slats tied with hinged clamps.

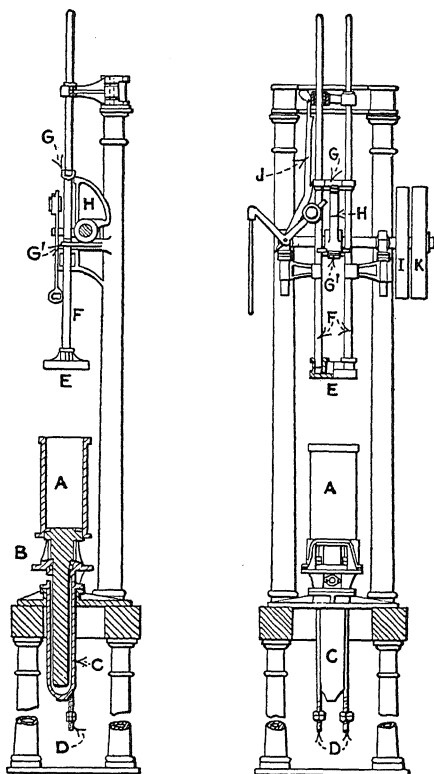
The machine requires 25 hp. with the auger shaft making 30 r.p.m. A man with two helpers makes 80 retorts per day. The retorts are air-dried for from 10 to 12 days, placed in the hot room for 50 days or more, and then baked as needed. A retort of St. Louis clay after 63 days in the hot room of 35°C., contained in one instance 0.95 per cent moisture at the top, 0.80 per cent at the middle, and 1.18 per cent at the bottom; the linear shrinkage was 3.5 per cent, the cubical 2.0 per cent, the porosity was 21.8 per cent vol.¹

3. *Dorr Hydraulic Press*.—The manufacture of retorts by means of

¹ Mühlhaeuser, *op. cit.*, p. 275.

the Dorr Press¹ embodies two operations, the hammering of pugged clay mixture into cylinders called ballots, and the molding of the ballots into retorts.

(a) *Hammering Machine*.—The hammering machine, shown in section and elevation in Figs. 95 and 96, is a small gravity stamp. The two leading parts are a cast-iron cylinder *A*, to receive the clay,



FIGS. 95 and 96.—Hammering machine.

which is closed at the bottom by piston *B* moving in hydraulic cylinder *C*, and a cast-iron stamp with head *E* shod with plank, two stems *F* joined by crosspieces *G* and *G'* (*G'* serving also as tappet), cam *H* attached to cam shaft with fast and loose pulleys *I* and *I'*, and latch finger *J* to hang up the stamp. The whole is mounted on a heavy cast-iron pedestal. In most modern machines a cast-

¹ French Patent No. 96,035, July 24, 1872.

iron single-frame stand is preferred to the double form shown in Figs. 95 and 96. The stamp is light, weighs about 100 lb., has a drop of 17 to 18 in., makes 70 drops per minute, compacts about 20 ballots per hour; usually, however, the work of a stamp is regulated by the needs of the press. One man attends the machine.

The clay containing about 15 per cent water is kneaded in a vertical bottom-discharge pug mill with die 8 in. in diameter, and the pug cut off in suitable lengths for the ballot machine.

In working the machine, piston *B* is lowered, some 8-in. pugged clay fed, the stamp unlatched and allowed to drop; feeding and stamping are continued until a ballot of the right size has been thoroughly compacted by about four blows; the stamp is hung up, and the ballot forced out of mold *A* by raising hydraulic cylinder *B*, and rolled over on a table; it is then righted and placed in a holder to be conveyed to the press.

With a dried cylindrical retort 57.56 in. long and 7.34 in. inner diameter, or an oval retort 57.57 in. long, 8.62 in. high and 6.91 in. wide, the ballots are 16 in. long and 14 in. in diameter, and weigh about 200 lb.

In some plants the hammer machine has been replaced by a powerful vertical bottom-discharge pug mill with balanced table.

(*b*) *Press*.—The inventor patented three types of presses. One with double compression has not been used at works.

The second,¹ called continuous or bottom-fed, has a capped vertical cast-iron steel core; clay filling cylinder is forced by an hydraulic piston into the space between cylinder and core; when the clay pipe has reached the cap, compression is stopped, the cap swung to one side, a slab of clay to form the bottom introduced and joined to the pipe; the cap is returned to its original position and bolted, compression started again to compact bottom and pipe. The retort formed is now pushed out at the top after the cap has been swung to one side, and then the lower end cut off with a wire.

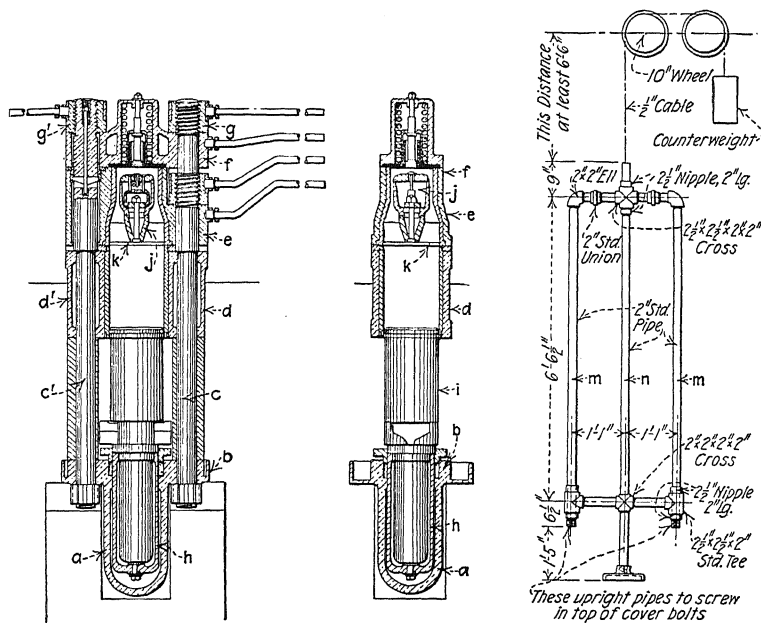
The pipe still in the machine now receives its bottom when the operation outlined is repeated. In this way several retorts are molded from one charge of clay. The machine is said to be in operation only at Ampsin, Belgium.

The new press of the Simonds Engineering Co., Lawrence, Kan.,² appears to belong to this type which has the advantage of requiring only a single hydraulic cylinder instead of the usual three, and

¹ Ill., Steger, *Zt. B. H., u. S. W. i. P.* 1900, XLVIII, 414.

² *Min. Ind.*, 1916, XXV, 773.

having thereby a simpler arrangement of valves. Figures 97 and 98 represent two vertical sections through the machine, and Fig. 99 an elevation of a retort guide. In Figs. 97 and 98, hydraulic cylinder *a* rests with its column *b* on the concrete foundation; columns *c* and *c'* connect cylinder *a* with receiver *d* and die *e*, and pass through the top piece *f* and nuts *g* and *g'*. Piston *h* with head *i* rises in the receiver *d* which is charged with a ballot of clay; the upper part of receiver *d* ends in die *e* which contains core *j*, bolted to the center of



FIGS. 97, 98 and 99.—Simonds hydraulic retort press.

four bars *k* cast solid with die *e*. Top piece *f* contains valve *g* for the passage of air. Die and top piece *f* swing on columns *c'*. Before starting piston *h*, receiver *d* receives its ballot of clay, die *e* and top piece *f* are swung into place and tightened with nuts *g* and *g'*. The ascending piston compresses the clay and forces it around the bars *k*; after passing, the slot in the clay is closed again when the mass is narrowed down to the thickness of the retort wall. When the closed end of the retort has been formed and sufficiently compressed, the movement of the piston is stopped, the nuts *g* and *g'* are loosened and the top piece *f* is swung to one side. The balanced retort

guide, Fig. 99, is now lowered that it may enclose the top of the retort, its fixed upright pipes *m* are screwed to the tops of the cover bolts, the central movable pipe *n*, connected by cable with a counterweight, is lowered, and piston *i* started. This is made to rise until the retort, steadied by the cap of the balanced pipe *n*, has been extruded to the desired length. It is then cut with a wire, encased

in a wooden mold, etc. Now piston *h* is lowered, die *e* swung to one side, receiver *d* charged with a ballot, die *e* swung back into place and then the top piece *f* after detaching the retort guide; the nuts are tightened, and the piston started again.

The third Dorr machine, called intermittent or top-fed, is the one which has come into general use. It is shown in vertical section in Fig. 100. The large cylinder *A* resting upon a cast-iron base-plate encloses its piston *B* which is connected through key *G* with plunger *C*; the latter terminates in detached punch *D* provided with poppet valve *E*. Twin cylinders *H* with pistons *I* connected by yoke *J* act upon annular plunger *K*, covered with copper and leather disks. The combined cross-sectional areas of *I* are much smaller than is the area of *B*. The stationary receiver *M*, firmly connected with columns *R* and *S*, is closed at the top by die *N* and

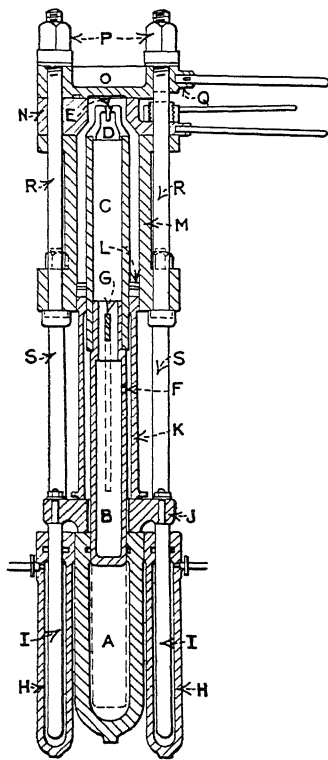


FIG. 100.—Dorr intermittent hydraulic retort press.

top piece *O* which are hinged around column *R* in such a manner as to allow at one stage swinging to one side, and at another locking with nuts *P* and *Q*. The upward travel of plunger *C* is automatically stopped by key *G* striking the ends of the grooves of *K* in which it travels; the air entering at *F* travels through grooves in *D*, passes by key *G* into plunger *C*, and leaves through poppet valve *E* into the vacuum formed. The figure shows the position of the pistons at which the retort, roughly molded, is to be forced by hollow

plunger *K* through die *N*. Supposing a retort is to be molded, punch *D* with its plunger *C* is allowed to recede to the lowest position, top piece *O* and die *N* are swung to one side to uncover receiver *M* so that the ballot can be introduced. Die *N* and top piece *O* are swung back into place and locked; the hydraulic pumps are started, they cause piston *B* and with it plunger *C* and punch *D* to rise until key *G* strikes its stop. Plunger *C* having been stopped, the hydraulic water passes through a four-way valve (not shown) into twin cylinders *H* in which pistons *I* are forced up and with them annular plunger *K*. When the roughly molded retort has been sufficiently compressed in about 2 min., the pumps are stopped, the pressure is temporarily released, and the top piece *O* unlocked and swung aside. The pumps are started again and, with plunger *C* in a fixed position, force out the clay between die *N* and punch *D*. Usually the rising retort is weighted by a circular balanced plate as in Fig. 99. The formation of a vacuum in the retort is prevented by air entering at *F*, passing into *C*, and through poppet valve *E*. When the retort has reached its proper length, the pumps are stopped, and the lower end of the retort cut off with a wire. The retort is enclosed in an oiled case, trimmed, the open end painted with grease, and removed. Now, punch *D* with plunger *C* and plunger *K* are lowered, die *N* is swung open around column *R*, the clay remaining in the receiver is removed, the press is swabbed with grease, and ready for the next ballot. The pressure exerted on the clay is about 2,000 lb. per square inch. Three to four men make 320 retorts in 6 to 8 hr.

Drawings of the Dorr press manufactured by C. Mehler, Aix-la-Chapelle, Prussia, have been published by Kahr¹ and by Liebig.²

The cost of a Belgian retort is about 50 cts.; an estimate by Johnson³ for the Central Western States is as follows: clay, \$0.0657; adobes, \$0.1220; supplies, \$0.0440; labor, \$0.2526; total, \$0.4843.

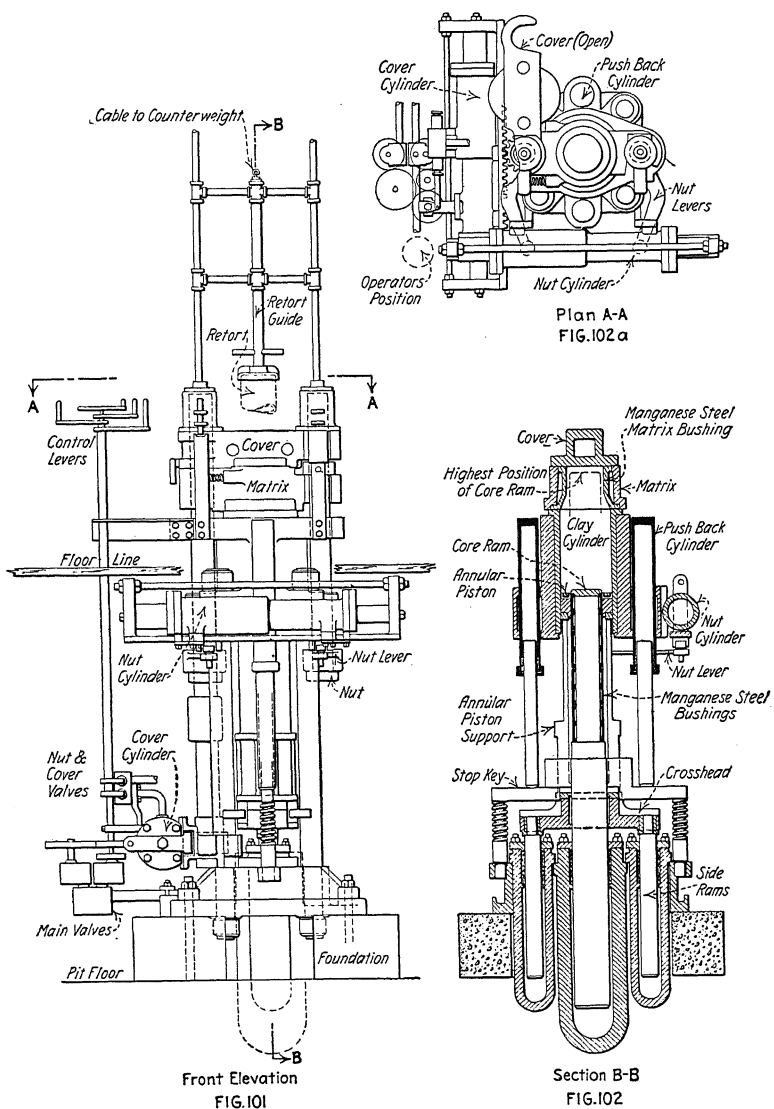
In the United States the hydraulic press of C. A. Wettengel has replaced to a considerable extent the machine of C. Mehler which used to be considered the best. It is shown in front elevation, vertical section, and plan in Figs. 101, 102 and 102a. Fundamentally the press is similar to that of Dorr shown in Fig. 100; it contains, however, a number of improvements which make the machine

¹ *Metall u. Erz*, 1913, x, 907.

² *Op. cit.*, 352.

³ *Loc. cit.*

more durable, more economical in operation and maintenance, effect a saving in labor, and furnish a better product.



FIGS. 101, 102 and 102a.—Wettengel hydraulic retort press.

Almost the entire press is made of steel, thus increasing the durability of the parts and eliminating cylinder breakage, further

all surfaces in contact with clay are easily and cheaply replaced, hydraulic flax packings having taken the place of troublesome leather; hydraulic cylinders serve for opening and closing the cover and matrix, and for tightening the bolts holding cover and matrix to the cylinder, thus doing away with the labor of one man whose work is arduous. The retort is superior, in that the pressure applied is twice that of the Dorr, that the core ram is the size of the inside of the retort and has no offsets which break the formation of the clay while the retort is being extruded from the press, and that the core ram does not penetrate the clay until this has first been compressed and entirely fills the clay cylinder and matrix. In the Dorr machine the core protrudes about 10 in. and penetrates the clay before this has been compressed so as to fill the space in the matrix, with the result that the clay ballot is cracked and the cracks have to be re-welded by pressure in extruding the retort.

Referring to the drawings, there are seen two horizontal hydraulic cylinders; the cover cylinder, Figs. 101 and 102a, placed at the base of the machine which serves for swinging the cover and the matrix in a horizontal plane; and the nut cylinder, Figs. 101, 102, 102a, placed beneath the floor line, Fig. 101, which serves for tightening and loosening the nuts placed at lower ends of the bolts. In regular operation, with the cover and matrix in open position, Fig. 102a, a clay ballot is placed in the clay cylinder, Fig. 102, the matrix and cover are swung into place above the clay cylinder, and closed by power applied to the cover cylinder; the closed position is shown in Figs. 101 and 102. Pressure is then applied to the vertical hydraulic cylinders at the base of the machine to raise together the core ram and the annular piston, maintaining the same relative positions as shown in the drawings. This forces the clay ballot into the matrix, it fills all the space in matrix and clay cylinder above the core ram and annular piston; the pressure applied is about 1,000 lb. per square inch. Now pressure is applied to the core ram, reaching 3,000 lb. per square inch, which causes it to penetrate the clay to the position indicated by the dotted lines in Fig. 102; this penetration displaces clay which moves into a space provided by the receding annular piston. The pressure is now released for an instant, and the nut cylinder, operating by means of the nut levers, made to loosen the nuts which hold the cover to the press. The cover cylinder is then swung aside to an angle of about 90 deg., as shown in Fig. 102a, so that the matrix is uncovered. The nut cylinder is made to tighten the cover bolts, and pressure

is again applied to the rams in the base of the machine, when the annular piston forces the retort out of the machine while the core ram remains in its highest position.

Valves are provided to admit air to the center of the core ram and into the retort to prevent its collapse caused by a partial vacuum that would otherwise be formed.

As the retort is being extruded, a guide shown in Fig. 101, is provided to steady it.

When the annular piston has reached its highest position, that is when it is flush with the lower surface of the matrix, the retort is cut off at the top surface of the matrix.

The pushback cylinders and rams are set in motion to return the core ram, and the annular piston, with attached parts to their starting positions; the cover cylinder is swung to an angle of 180 deg. from its original position and the matrix to the position just previously occupied by the cover. In this position, the ring of clay remaining in the matrix is removed. Another ballot of clay is placed in the clay cylinder; the machine is ready to repeat the operation just described.

For a press there are provided, a pug mill which makes a round bar of clay of 13 to 14 in. in diameter containing less than 13 per cent water, and a machine which cuts the bar into ballots 18 to 20 in. in length. The press makes a retort in 40 sec. Three men are required, one operating the pug mill and delivering the ballots to the press, one press operator, and one finisher and trucker who make 300 retorts daily. A retort weighs 130 to 140 lb.

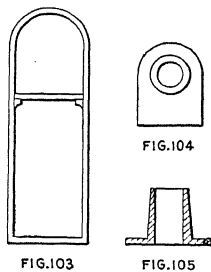
Queneau¹ has devised a method for making composite retorts consisting of three layers, of which the inner and outer are to resist the harmful effects of charge and fire, and the central to form the body of the retort. The method has been tried but has been given up.

A comparison of the three methods of making retorts shows that the hydraulic press furnishes the best product the hydraulic retort contains the least water and shows the greatest density; it is strong and can have thin walls, absorbs little zinc and is not readily corroded; it has a long life, can stand a high temperature and thus permits forcing a charge to give up its zinc. In spite of the higher cost of manufacture in comparison with the auger machine, the advantages are so great that it is superseding the latter, at least in large plants.

¹ *Eng. Min. J.*, 1906, LXXXII, 677.

At Angleur, Belgium¹ there were required in 1840 about 17 hand-made retorts per ton of spelter, and in 1888 only 1.7 auger retorts. The life of a hand-made retort is 25 days, of an auger retort 40 days, and of a press retort 60 days. The auger retort with 16 per cent water requires from 6 to 7 days to become saturated with zinc, the press retort with 7 per cent water only 2 days; the yield in spelter with a press retort is 5 to 6 per cent greater than the auger retort.²

82. Molding of Muffles.—Muffles are used only in Silesia, even there they have been largely replaced by oval retorts. The muffle, shown diagrammatically in Figs. 103 to 105, has in the upper part at the front two projections for the support of a brick bridge-piece which divides it into two parts; the upper is closed by a clay tile with collar over which is slipped the inclined cylindrical condenser, the lower by clay slab. The muffles are molded on end and on the bottom.



FIGS. 103, 104 and 105.—Silesian muffle.

1. Molding on End.³—The mold is made up of three lengths, each divided longitudinally into two parts which are held together by iron straps and screw bolts. The central length has pins or tongues which fit into holes or grooves in the adjoining parts. The bottom-length is placed vertically on a base-board, a slab of clay is beaten down with a stamper to form the bottom with up turned sides, these are cut off at a slant to furnish a large surface and roughened by making with a stick parallel indentations that they furnish a good support for the sides. These are clay slabs which are joined to the bottom and beaten against the mold with paddles. The middle-length is placed upon the first, joined to it, and molding continued; lastly comes the top-length. When molding is finished, the bridge pieces are attached.

2. Molding on Bottom.⁴—The mold consists of three parts, the base-board, the side-board, and the center piece. The bottom of the muffle is prepared by cutting into a thick slab of clay an oblong cavity having the inner dimensions of the muffle; the side-boards are

¹ Batault, *Bull. L'Ind. Min.*, 1888, II, 515; *Berg. Hüttenm. Z.*, 1889, XLVIII, 390.

² Oueneau, *Eng. Min. J.*, 1906, LXXXII, 677.

³ Thum, *Berg. Hüttenm. Z.*, 1859, XVIII, 405, Plate XVI, Fig. 3.

Percy, "Metallurgy," 1861, p. 558.

⁴ Georgi, *Berg. Hüttenm. Z.*, 1877, XXXVI, 71.

put in place and covered with slabs of clay, care being had to join sides and bottom and beat the clay against the side-boards. The clay bottom is covered with a board, the wooden center put in position, and the roof molded. The center piece is sometimes covered with moistened sacking.

The muffles remain 3 days in the mold, when they will have come to a set and be sufficiently strong to stand alone.

3. *Other Methods of Molding.*—The methods of Wernicke and machine-molding are discussed by Steger.¹

Muffles last about 40 days.

83. *Drying of Retorts.*²—Hand-made and auger retorts contain about 16 per cent, and pressed retorts 7 per cent water; this is expelled in drying houses in 6 weeks or more. A drying chamber usually has a latticed floor and is heated by steam pipes under the floor or radiators in the chamber, the moist air is drawn off usually by natural draft through flues in the roof. In the first chamber a temperature of about 30°C. is maintained, in the second it is raised to as much as 70°. A retort remains in the first chamber about 3 weeks, and from 3 to 6 weeks or longer in the second. The retorts are placed vertically open ends upward with sufficient spaces between to allow free circulation of air; they ought to be protected from draft. The floor area allowed is about 1 sq. ft. per retort excluding the room required for alleys to furnish access to the stacks. Even in a small plant the floor space covered by drying rooms is large. In some instances two-story dry houses are found. Drawings of the pottery of the New Jersey Zinc Co. at Palmerton, Pa., have been published by Fiske.³ It is, however, preferable to have dry rooms on one floor, as there is less handling. A number of small rooms is preferable to a few large ones. It is essential that the ground of the drying room be thoroughly drained, and that there be sufficient space underneath the floor to allow making repairs for leaks in steam pipes. The dried retorts are removed to a storage place which is usually situated in the distillation building near the annealing ovens.

84. *Glazing of Retorts.*⁴—At some works the dried retorts are painted with a readily fusible mixture before they are baked, so as to fill the pores and thus diminish the egress of zinc vapor from

¹ *Zt. B. H. S. W. i. P.*, 1900, XLVIII, 419.

² Neuray, *Rev. Un. Mines*, 1919, II, 553.

³ *Tr. A. I. M. E.*, 1917, LVII, 868.

⁴ Mühlhaeuser, *Metall u. Erz*, 1918, XV, 393.

and the ingress of fuel gases into the retort. The mixture is applied either outside or inside, often on both sides. Such a mixture is made up of clay, glass or quartzite and soda, *e.g.*, 60 lb. clay, 30 quartzite, 10 soda, or 60 clay, 40 iron blast-furnace slag, 20 soda.¹ A glaze is also made up of fluorspar and zinc sulphate; after the fluorine has been expelled the retorts assume a very dense surface;² Mühlhaeuser,³ gives analyses of glazes.

Retorts often become glazed in the furnace on the outside with a green coat from the Fe_2O_3 in the coals combining with the SiO_2 and Al_2O_3 of the clay; such a glaze cannot form when natural gas is the heating fuel.

85. Baking of Retorts.⁴—The object of baking retorts is to drive off the chemically combined water, to strengthen them and to change their character that they may be transferred red-hot from the oven to the furnace which is at a white heat. The clay mixture resists impact and change of temperature readily when the bonding clay has lost its water, but has not yet begun to shrink, and the fluxing material still remains inactive. Mühlhaeuser,⁵ heating progressively a sample of retort material found that from 14° to 376°C . it lost its hygroscopic water and organic matter, that between 376° and 660° the chemically combined water was expelled, and that between 660° and 781° the further loss in weight was very small. The temperature of the baking oven is held at about 800°C .; the baking of a lot of retorts takes about 24 hr., half the time is taken up by charging, heating up, and cooling.

The oven is a brick chamber with tile floor having square or oblong openings spaced so as to leave room for the retorts to be placed upright between them. The fireplace with up-draft ovens is placed beneath the floor when the hot gases pass upward encircling the retorts; with down-draft ovens it is placed to one side, when the hot gases strike the roof, are deflected, descend along the sides of the retorts, and pass through the floor into a main flue. Down-draft ovens are preferred to up-draft, as they give a more uniform heat. Sketches of up-draft and down-draft ovens are given in Figs. 106–109 and 110–112. With down-draft ovens fired with natural gas, the burners enter at one side beneath the arch. The dried

¹ Juretzka, *Metall u. Erz*, 1913, x, 82.

² Babcock, *J. Am. Cer. Soc.*, 1919, II, 85.

³ *Op. cit.*

⁴ Mühlhaeuser, *Metall u. Erz*, 1918, xv, 202.

⁵ *Zt. angew. Chem.*, 1903, p. 275; *Thonind. Z.*, 1903, xxvii², 2,018.

retorts are placed in an oven about 2 hr. after the last batch has been drawn; the door is closed and luted, and the heat of the oven walls allowed to act about 15 hr. upon the retorts; the fire is then kindled, the heat brought to 800°C . and held there about 12 hr.

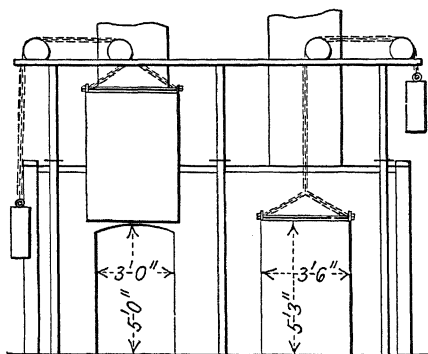


FIG. 106

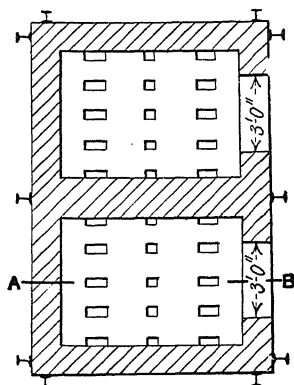
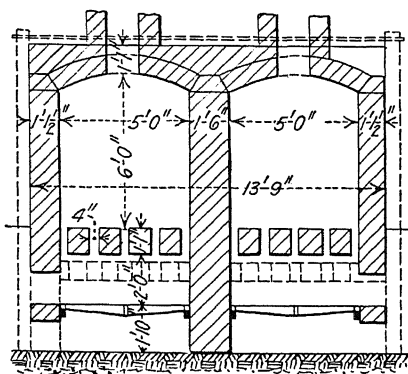
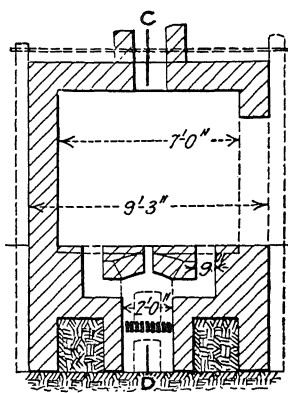


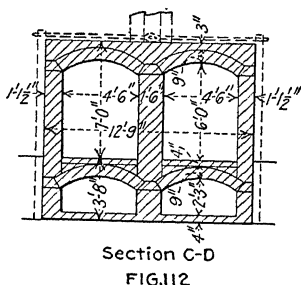
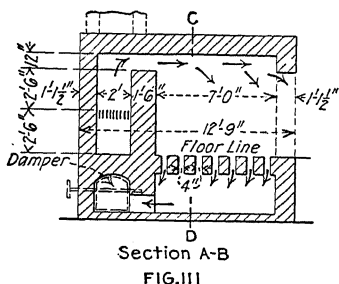
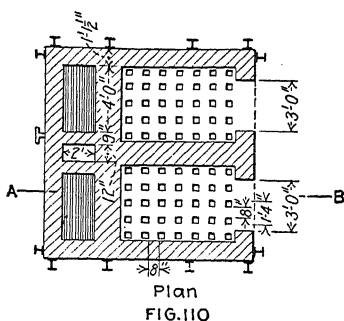
FIG. 107

Section C-D
FIG. 108Section A-B
FIG. 109

FIGS. 106-109.—Double up-draft baking oven.

The baked retorts are taken out red-hot from the oven to replace defective ones in the distilling furnaces. A retort is seized with a pair of tongs at the open end by one man and drawn out of the furnace; an iron pipe is inserted by another and the lower end raised with a bent iron bar by two men; this bar the goose-neck or retort carrier is shown in Fig. 113; three men carry the retort to the dis-

tilling furnace. Here two men raise the closed end to the shelf of the pigeon-hole, when the third man pushes it in on to the back support covered with a layer of non-refractory clay which sinters and holds in place the retort. Instead of transferring in the open a



FIGS. 110, 111 and 112.—Double down-draft baking oven.

baked retort with goose-neck carrier to the distilling furnace, two baked retorts are placed in a pair of sheet-iron cylinders resting on a two-wheeled hand truck and moved to the furnace; each cylinder is made up of two concentric circular pieces of sheet iron separated by asbestos. The retort cools in its passage from the baking oven to the distilling furnace and is here heated suddenly to $1,300^{\circ}\text{C}.$, which causes a crackling of the surface. The high temperature causes considerable shrinkage. In a baked retort with 28 per cent pore space¹ and 1.92 sp. gr., the pore space was reduced to 24.5 per cent and sp. gr. increased to 2.0.



FIG. 113.—Goose neck of retort carrier.

¹ Mühlhaeuser, *loc. cit.*

Figure 114 gives the side elevation of a retort *m*, with clay condenser *o* and sheet-iron prolong *p*, supported at the back with closed end on a ledge *n*, at the front with open end on a firebrick tile *r*, the continuation of which forms a cast-iron plate *q*; a tile and plate are supported by firebrick tiles and cast-iron frames placed

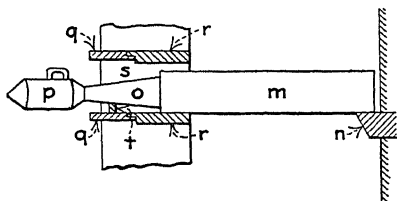


FIG. 114.—Section through furnace with retort in place.



FIG. 115.—Clayton condenser support.

at such distances as to enclose two retorts; the space around the retorts being luted with clay. The condenser, luted to the mouth of the retort is supported toward the front by a brick piece *t*; the prolong is slipped over the nose of the condenser. The brick piece has been replaced in many instances by the Clayton adjustable iron support shown in Fig. 115.

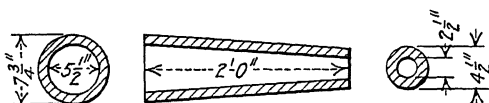


FIG. 116

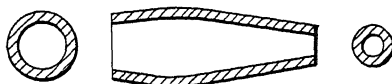


FIG. 117

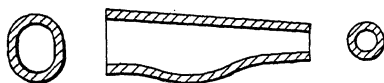


FIG. 118

FIGS. 116, 117 and 118.—Belgian condensers.

86. Manufacture of Condensers.—The clay condensers which are to collect the condensed zinc vapor have various forms. Leaving out the knee-shaped Silesian form¹ which has become obsolete,

¹ Percy, "Metallurgy," 1861, p. 558.

there are in use at present two types, the Belgian shown in Figs. 116 to 118, and the Rhenish represented by Fig. 119. The clay mixture for making condensers is usually less refractory than the one used for retorts, as a condenser is situated outside of a distilling furnace and not subjected to a high temperature.

In some instances, *e.g.*, at Palmerton, Pa., the mixture used is the same as that with the retorts, because it has been found that the longer life of the better condenser more than makes up for the difference in cost of material.

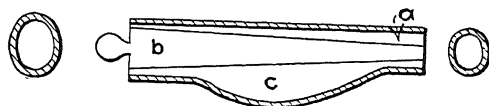


FIG. 119.—Rhenish condenser.

The Belgian condenser used to have the form of a truncated cone, as shown in Fig. 116; in order to furnish a receptacle for the zinc it has received the form of two truncated cones joined at their bases, Fig. 117; this is emphasized in Fig. 118 where the lower side is bellied. The length of a condenser is 17 to 24 in.; the smaller diameter $2\frac{1}{2}$ to 3 in., it has to be large enough to permit introduction of a spoon or scraper to remove zinc or accretions; the large diameter has to correspond to the mouth of the retort; the wall is $1\frac{1}{2}$ in. thick.

Table 29¹ gives some recent measurements.

TABLE 29.—SIZES OF CONDENSERS

	Inches
Outside diameter of large end.....	7 to $7\frac{1}{2}$
Inside diameter of large end.....	$6\frac{1}{4}$ to $6\frac{3}{4}$
Outside diameter of small end.....	$4\frac{1}{8}$ to $4\frac{5}{8}$
Inside diameter of small end.....	$2\frac{5}{8}$ to $3\frac{1}{8}$
Thickness of wall.....	$\frac{3}{4}$
Length.....	17 to 20

The size and form of a condenser depend upon the volume and temperature of zinc vapor and gas passing in a given time, and the material of construction (iron, clay); vapor and gas enter the condenser at $1,050^{\circ}\text{C}$., the gas leaves at 600°C . Snyder² states that a conical clay condenser of the Belgian furnace offers 1 sq. cm. cooling surface for each 0.4 g. zinc vapor condensed per hour, has a

¹ Johnson, *Met. & Chem. Eng.*, 1917, XVI, 477.

² *Tr. Am. Electrochem. Soc.*, 1911, XIX, 317; *Mct. Chem. Eng.*, 1911, IX, 265.

thickness of wall which permits 0.21 Cal. to flow per hour through 1 sq. cm. surface at $725^{\circ}\text{C}.$, and a form for which the product of velocity of gases in centimeters per second and average diffusion distance (corrected to $864^{\circ}\text{C}.$) in centimeters is $9\frac{1}{2}$. He makes these data the basis for the construction of condensers for electric furnaces in which the amount of zinc vapor delivered is 300 or 400 times as great as in a retort.

A condenser costs about 5 cts.; there is required one condenser per day for every 11 to 12 retorts in a furnace. Assays by Johnson¹ show that old condensers contain 35.5 per cent Zn.

Formerly condensers were made by rolling a slab of clay, $\frac{3}{8}$ in. thick, over a wooden die, joining the edges and cutting off the ends.

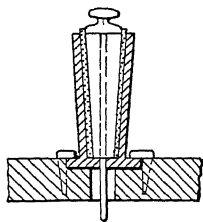
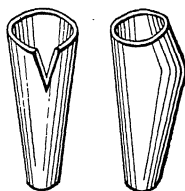


FIG. 120.—Cast iron frame for hand-molding condenser.



FIGS. 121 and 122.—Hand-molding of condenser with belly.

Later the work was simplified by the use of a cast-iron mold clamped over an opening in the working table, Fig. 120. A loaf-shaped piece of clay was dropped into the greased mold, and a wooden mandril, with iron head and central projecting rod, forced in by hand with a rotary motion, the hole in the bottom of the mold serving as a guide for the projecting rod. When the mandril had been pushed home, the exuding clay was cut off, the mandril withdrawn, and the mold inverted when the condenser dropped out; a man made 200 condensers in 10 hr.

In making a condenser with a belly, a single cone, with larger diameter than desired, was molded in the usual way, allowed to dry for a day, and a V-shaped piece was cut out, Fig. 121, the sides were then drawn together and joined, Fig. 122. In making a double cone condenser, both ends were cut and drawn in.

Instead of forcing in the mandril by hand which was the common practice until about 1905, a weighted mandril came into use. This is shown in Fig. 123 which is self-explanatory. This apparatus was

in use at La Salle, Ill.; a man made 250 condensers in 10 hr. A front elevation of the one-man machine in use there at present is given in Fig. 124. Cast-iron columns, tied at the tops by crosspieces and bolted at the bottoms to the upper flanges of two heavy I-beams, form vertical guides for the up- and down-movement of a crosshead carrying a revolving mandril. To the lower flanges are bolted hangers carrying the shaft of a pair of cogwheels which by means of crank pins and connecting rods impart the up- and down-motion of the crosshead. The shaft of the mandril is rotated by a separate pulley acting through bevel gears and a groove and spline. The columns are connected near the bottom by a narrow cast-iron table carrying a pair of condenser molds attached to a short vertical

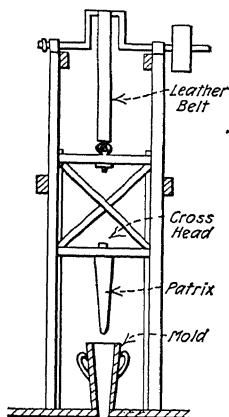


FIG. 123.—Early machine for molding condenser.

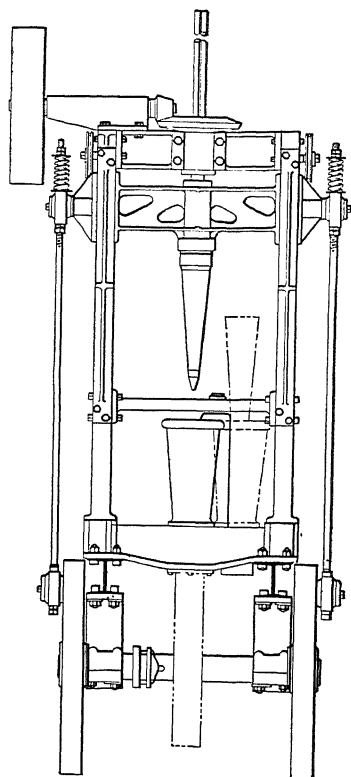
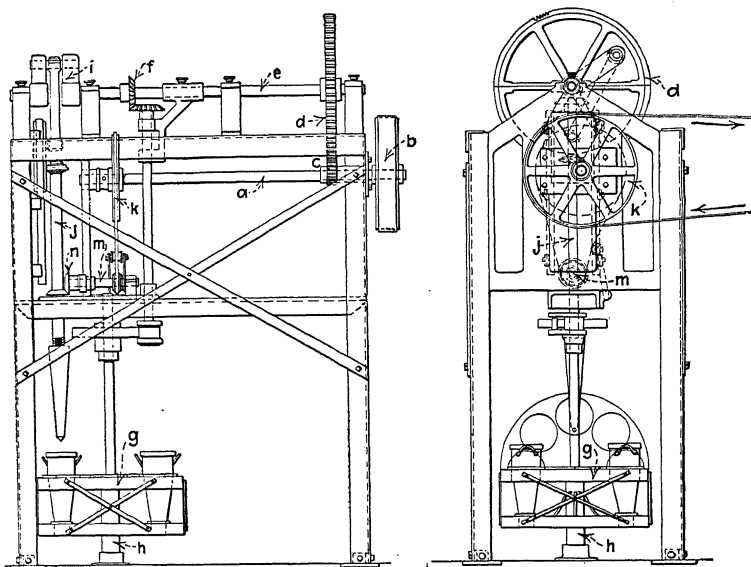


FIG. 124.—Improved one-man machine for molding condenser.

shaft in a crosspiece. The cogwheels are driven by pinions not shown. In molding condensers, one mold in place under the mandril is oiled and charged with the ballot of prepared mixture; the rotating mandril descends, forms a condenser and causes the excess clay to extrude and fall into the chute for excess clay. The mandril rises and when it has left the mold, the pair of molds is swung by hand through an angle of 180 deg. to a stop; this brings the mold with

the condenser over the ejector-pump which, driven by compressed air, forces the condenser out of the mold to be placed to one side. The pair of molds is now swung back through 180 deg. to a stop when the empty mold will arrive under the plunger and the filled mold under the ejector. In this way, one mold is being filled at the same time that the other is being emptied. One man makes 500 condensers in 8 hr.



FIGS. 125 and 126.—Garrison-Whipple condenser machine.

With the increase of size of plant, molding machines of large capacity have been constructed. Two, those of Garrison-Whipple and of Stafford may serve as example.

The Garrison-Whipple condenser and Ball machine¹ enables one man with helper to make 2,000 condensers in 10 hr. Often a day's work of four men working 6 hr. and using only half of the molds amounts to 2,500 condensers. The Ball machine is a small pug mill which kneads the clay, forces it into a ball-shaped mold, from which the clay ball of the size necessary to form a condenser is ejected intermittently. The condenser machine, shown in side and end elevation in Figs. 125 and 126, consists of a rotating vertical

¹ Garrison, *Eng. Min. J.*, 1910, xc, 722; Cherryvale Iron Works, Cherryvale, Kan.

plunger, *j*, with conical die and rotating horizontal table, *g*, holding the molds; the motions of plunger and table are so correlated that before every downward movement of the plunger the table is rotated to have in place beneath the descending die an empty mold charged with a ball of clay. The figures show an oblong steel frame tied at top center, and braced on two sides. It carries the main driving shaft, *a*, with pulley, *b*, 30 by 6 in., making 56 r.p.m. Shaft *a* has pinion *c* which drives large cog wheel *d*; shaft *e* of the latter carries miter wheel *f* for rotating by gearing molding table *g* carried by center post *h*, and double crank *i*, for giving plunger *j* a reciprocating motion; shaft *a* carries at the further end sprocket wheel *k* and chain, which revolves countershaft *m* and rotates plunger *j* by means of miter gear *n*. Molding table *g* carries eight molds which fit each with keys into slots and are prevented from spinning. A water attachment on the frame (not shown) sprays a given amount of water on to the die. The machine requires 10 hp. and makes eight condensers per minute, *i.e.*, the molding table must make 1 r.p.m. In working, molds and die become polished in a short time, and clay does not adhere to them. In starting, these parts have to be frequently oiled (castor machine-oil diluted with 20 per cent kerosene); this has to be done also when the machine is to remain idle for a while. The clay ball received from the balling machine is charged in form to a cylinder or cone by throwing forcibly on a table that the striking side may be expanded. It thus fits better into the mold, and the clay is more uniformly spread in the mold by the die than would otherwise be the case.

The Stafford machine¹ made by the Union Iron Works, Iola, Kan., is shown in Fig. 127. The principle of molding is similar to that of the Garrison-Whipple, the mechanism, however, is different. The cast-iron base, *a*, carries a frame consisting of the rear end, the center, and the table-end supports, *b*, *c*, *d*; the frame carries driving shaft *e*, which receives its power through fast pulley *f* with loose pulley *f'*; shaft *e* carries worm *g* and bevel gear *m* meshing with *n*, the latter has a spline which enters groove *o* in plunger shaft *p*. The worm *g* engages wormwheel *q*, carried by bracket *r*, which through stroke arm *s*, connecting rod *t*, and crosshead *u* gives plunger arm *p* an up- and down-motion. Crosshead *u* travels in guides *v* and is rotated at the same time by bevel gears *m* and *n*. Crosshead *u* strikes on its upper movement table-turning bar *w*, pivoted at one end and carrying at other rod *x*, connected with bell

¹ Photograph, *Eng. Min. J.*, 1919, CVII, 706.

crank *y*, pivoted on center support *c*. Crank *y* gives table-hook-arm *z* a reciprocal motion which by means of ratchet *r* strikes bevel pinion *2* on bottom of plate *3*, and rotates it. Bottom plate *3* and top plate *4*, connected by pipe spacers *5*, form the rotating

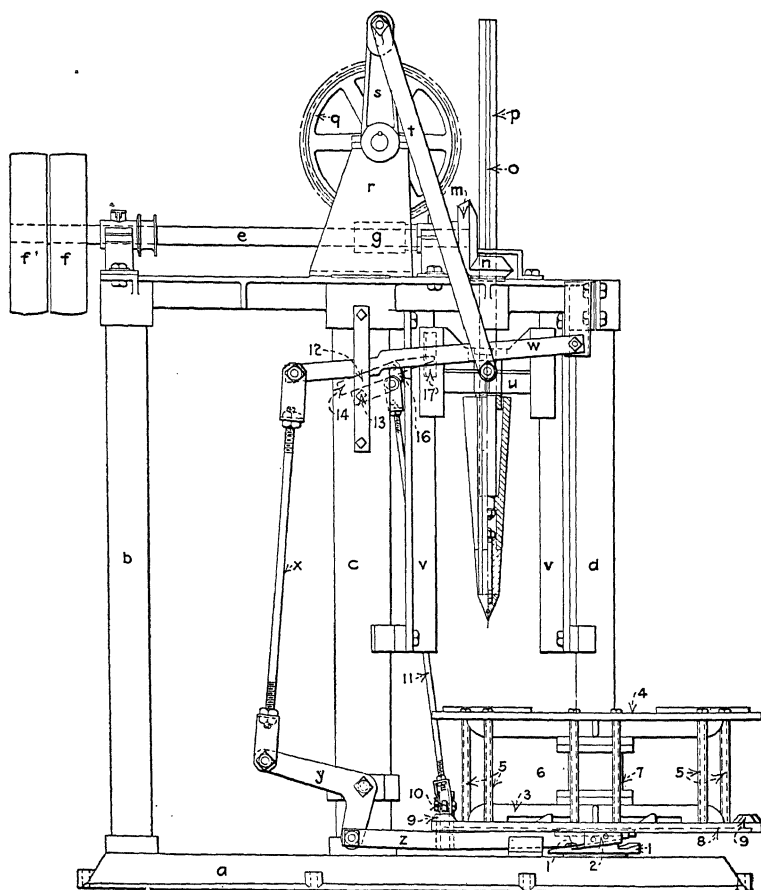


FIG. 127.—Stafford condenser machine.

molding table *6* carried by spool *7*, enclosing table-end support *d*. The sheet-iron molds are slipped over cast-iron collars on bottom plate *3*. Beneath bottom plate *3* is cast-iron ring *g* with catches *9*, which receive latch *10* and stop the rotating table. Latch *10* is connected by rod *11* with bell crank *12*, pivoted on *13*, and with latch lifting lever *14* by means of elbow *16*. Clip *17* for crosshead

raises and lowers lever 14 and thus gives rod 11 the necessary reciprocal motion to raise and lower latch 10.

Driving shaft *e* makes 175 to 200 r.p.m. The machine requires $2\frac{1}{2}$ hp., makes 800 condensers in 10 hr. and is served by two men. When a condenser has been molded, it is allowed to air-dry for from 1 to 3 days, and is then trimmed; the larger base is turned up or crimped by pushing into a sheet-iron form or ring, 6 in. high, which gives it the size of the mouth of the retort; this crimping also causes bellying of the central part.

The Rhenish condenser, Fig. 119, is 27 to 39 in. long, 4 to 6 in. wide, has a wall $\frac{1}{2}$ to $\frac{3}{4}$ in. thick and weighs air-dried 50 to 60 lb. A slab of clay is wrapped around a wooden three-piece mold which has been dusted with finely ground brick; the clay is pressed on to the mold, the edges are joined, and the ends trimmed. After a new condenser has come to a set in 24 hr., the central wedge-shaped part of the mold is withdrawn, and the collapsing other two are removed. A mold of two pieces has replaced in many instances the one of three.

Condensers, after air-drying for several days on shelves, are white-washed with milk of lime in order to facilitate the removal of adhering incrustations. They are then transferred to a kiln to be baked. In a kiln they are placed on end in rows with large and small ends pointing downward alternately so as to fill the space completely. A kiln will hold as many as 1,000 condensers. It is brought to the baking temperature of 900° to $1,000^{\circ}\text{C}.$; the condensers bake about 18 hr. After cooling, they are transferred to the storage place. In a down-draft kiln the condensers at the top are likely to be brownish, lower down white, and at the bottom to have a pinkish color.

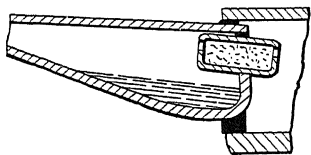


FIG. 128.—Primrose condenser.

Primrose¹ has constructed a special form of condenser with fume filter which is to hold back any lead fume that is carried over by the zinc vapor. It consists, Fig. 128, of a conical 10-in. fireclay tube, packed with firebrick chippings, which is inserted into the larger end of the condenser. The velocity of the fume is sufficiently retarded to cause the lead to become entangled, while the zinc passes through. The lead collects on the bottom and is poured off at intervals. If the filler is inserted in the smaller end of the

¹ *Eng. Min. J.*, 1910, xc, 418.

condenser, it holds back much of the zinc which will otherwise pass off as blue powder.

The carbonaceous filter of the Hopkins fumeless zinc process¹ is made of coke instead of pieces of brick. It is to counteract oxidation of zinc vapor by air.

Shortman² has placed over the mouth of a retort treating galvanized residues, a fireclay sleeve packed with anthracite or coke in which the lead is condensed, while zinc, 99.9 per cent pure, passes over.

Besides the clay mixtures for retorts and condensers there has to be provided furnace mud for luting purposes. This is a pugged mixture of low-grade clay and coal which should be lean so as not to burn hard; if hard, it would be difficult to cut out.

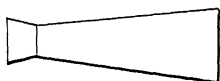


FIG. 129



FIG. 130



FIG. 131

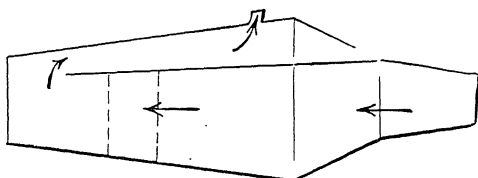


FIG. 132

FIGS. 129-132.—Prolongs.

87. Prolongs.—A prolong is a sheet-iron tube, 2 to 3 ft. long, which is slipped over the nose of the condenser; it is to collect the blue powder that passes off from the retort, especially at the beginning of the distillation. A few simple forms used with Belgian and Rhenish retorts are shown in Figs. 129 to 132; more complicated forms are given by Steger.³ Formerly prolongs were little used in the United States, as by shutting off the flame they hindered the furnace man from observing the working of a charge, and as the recovery of metal was not considered sufficient to pay for the outlay and trouble. At present most retorts are provided with prolongs

¹ Bannister, *Jour. Inst. Met.*, 1910, III, 213.

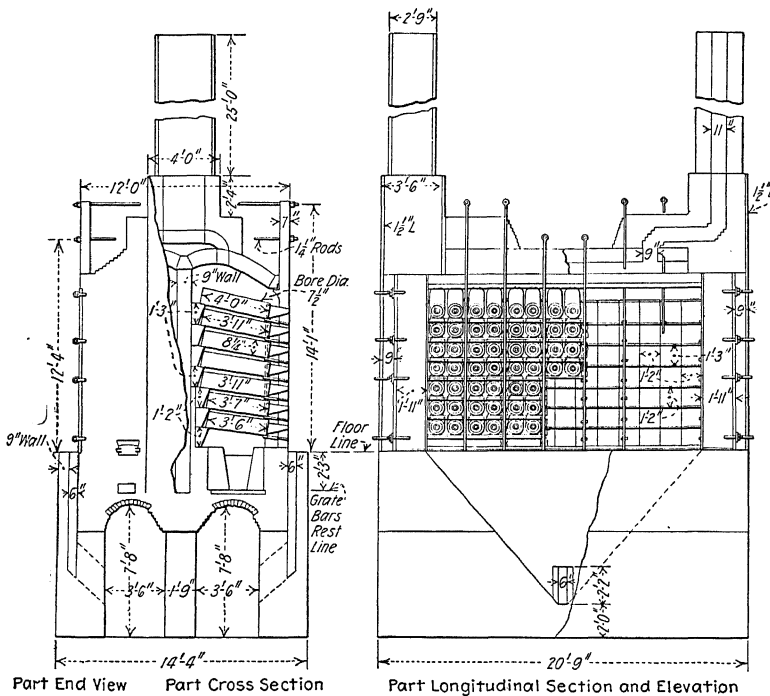
² *Met. Ind.* (England), 1912, IV, 355; *Jour. Inst. Met.*, 1913, IX, 247.

³ "Metalldämpfe in Zinkhütten," Enke, Stuttgart, 1896.

especially, since the production of cadmium has been started; most of the cadmium of the charge is collected in the blue powder. The recovery of zinc in using a prolong is about 3 per cent greater than without it.

BELGIAN METHOD OF DISTILLATION

88. Introduction.—The characteristics of this method are the use of a flame-heated shaft furnace with from four to eight, usually six, rows of retorts supported at the ends and sloping slightly toward



FIGS. 133 and 134.—Belgian furnace, Joplin, Mo.

the front, the number of retorts in a row being eight in the older and reaching 72 in the newer furnaces.

The furnaces are either single or double, *i.e.*, they have either a single shaft-like heating chamber, or two placed back to back against one dividing wall. A small single furnace will contain $8 \times 6 = 48$ retorts and its double type $2 \times 48 = 96$ retorts. Large furnaces are always double. Such a furnace, *e.g.*, will have on a

side $4 \times 6 = 24$ retorts in a section which is bounded by buck stays or stanchions; there are 18 sections on a side, $18 \times 24 = 432$ retorts; or 864 retorts in a double furnace. The length and height of a furnace is seen to vary with the number of retorts; the width, however, is more a constant, owing to the limited length of a retort.

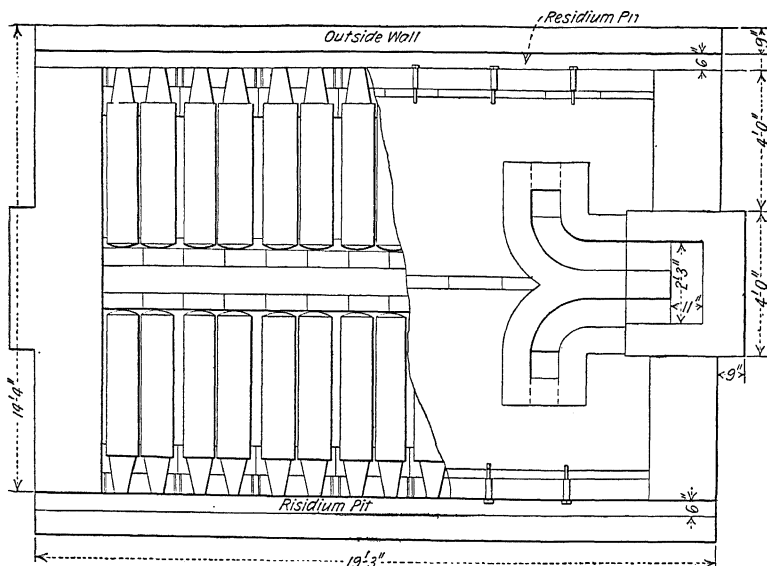


FIG. 135.—Plan.

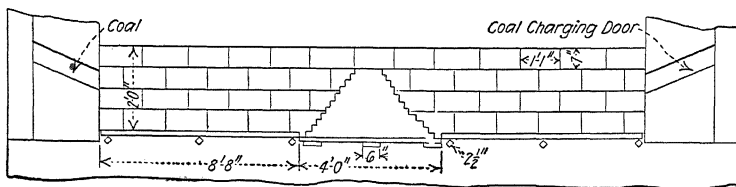


FIG. 136.—Section through fire box.

The following details are taken up in connection with Figs. 133 to 136:

The back of the furnace (Fig. 133) is a solid wall of firebrick with ledges for support of rear ends of the retort. The front is a pigeon-hole wall, each pigeon-hole or niche, 28 by 15 in., holding two retorts, Fig. 134. The wall is made up of eight, Fig. 134, rectangular cast-iron stanchions let into the brickwork at the bottoms and tied by rods at the tops; a stanchion, 7 in. wide by $1\frac{1}{4}$

in. thick, Figs. 133 and 134, has ribs on the sides for the support of inclined cast-iron plates which carry the props of the condensers, back of the stanchions are placed vertical brick tiles, 9 in. wide, which carry inclined firebrick slabs forming the continuations of the cast-iron plates and supporting the open end of the retorts. In order to give the necessary strength to the brick hearths, either the horizontal slabs are bonded, as shown in Fig. 137, or the vertical tiles form continuous columns and carry the firebrick slabs on projections Fig. 138 (see also Fig. 144). The outer cool part of the furnace is therefore made up of cast-iron parts, while their continuations toward the hot interior are of firebrick. The stanchions, Fig. 133,

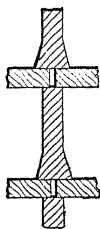


FIG. 137.—Horizontal slabs in pigeonhole wall.

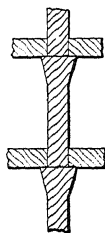


FIG. 138.—Vertical slabs in pigeonhole wall.

have above the top row of retorts lugs which carry cast-iron skew-backs for the support of the roof. The open spaces between a pair of retorts in a pigeon-hole or niche are plastered with clay.

Furnaces are fired direct with bituminous coal or anthracite, in the latter case under-grate blast is necessary; with oil, producer gas or natural gas. Fuel dust has been tried. It has proved¹ satisfactory as long as the ash content did not exceed 3 per cent; dust with more ash glazed and then slagged the retorts. As coal with as little as 3 per cent ash is difficult to obtain, dust firing has not been economically successful. The heat in the gases issuing from the furnace goes to waste or is utilized in waste heat boilers; it is returned to the furnace by recuperative or regenerative systems.

Forty or fifty years ago¹ the Belgian furnaces contained from 50 to 90 small retorts of about 0.8 cu. ft. capacity each; at present they contain from 500 to 700 larger retorts with a capacity each of 1.4 cu. ft. The life of a retort in 1844 used to be 20 days, at present is 30 to 40 days. With hand-firing there were required 3 to 4 tons of coal per ton of ore, with gas-firing this has been reduced to 1.50

¹ Stone, *Tr. Electrochem. Soc.*, 1914, XXV, 16; *Met. Chem. Eng.*, 1913, XI, 677.

to 1.75 tons, and with regenerators even to 0.9 ton; in addition, gas-firing has increased the life of the retort and the yield of metal. Labor required was 5 days per charge, that is two 24-hr. men and one helper on day shift only. As the old furnaces worked only a ton of ore, they required 5 days of labor per ton of ore. At present 24-hr. work has been done away with, and not over 1.5 days labor is required per ton of ore. The yield in zinc in 1844 used to be 62 per cent, in 1880 a good yield gave 75 per cent, at present 87 per cent is considered fair, and 90 per cent good. Thus considerable progress has been made in the distillation of zinc ores by improvements in the construction and method of firing of furnaces, in the manufacture of retorts, in the handling of materials, and in the recovery of metal.

There exists a great variety of Belgian furnaces, the present discussion will be confined to five types; one fired direct of Joplin, Mo.; three fired with producer gas, of which the Matthiessen and Hegeler has waste-heat boilers, the Convers De Saulles recuperators, and the Neureuther regenerators; and one fired with natural gas.

89. Furnace of Joplin, Mo., Direct-Fired.—This furnace is shown in Fig. 133, part end elevation and cross-section, Fig. 134, part side elevation and longitudinal section, Fig. 135, part plan and horizontal section, and Fig. 136, section through firebox. It is a double furnace which has seven rows of retorts each with 14 vessels, or 98 retorts on a side, equal $2 \times 98 = 196$ retorts in all. The furnace occupies a floor space 20 ft. 9 in. by 14 ft. 4 in., is 14 ft. 1 in. high from floor line to top, extends 10 ft. 9 in. beneath the floor line, and has at either end a brick chimney base 48 by 42 in. and 28 in. high with a chimney 27 by 11 in. inside and 25 ft. high. A base rests in part on the end wall of the furnace, in part on a pier built up from the ground. Furnace and chimneys are tied cross and lengthwise by iron rods, the corners are enclosed in angles.

The fireplace, Fig. 133, is 2 ft. 3 in. deep; it contains two sets of grate bars separated by a fire bridge, Fig. 136. A set has three bars, 8 ft. 8 in. long and 2 in. square, supported by $2\frac{1}{2}$ -in. crossbars; the fire bridge, 4 ft. wide at bottom, is carried by 6-in. cast-iron plates. The grate, Fig. 133, is 8 ft. 8 in. above the bottom of the ash pit which also receives from the cinder pockets, extending the length of the furnace, the residues of the retorts. At the ends of the furnace are coal-charging doors, Figs. 133, 136, and beneath these poking doors, Fig. 133, to loosen clinkers. The top of the coal on a grate is about 15 in. below the bottom row of retorts. The grate area, $2 \times 0.5 \times 8$ ft. = 8 sq. ft., heats a combustion chamber of

558 cu. ft. with 98 retorts or 1 sq. ft. grate area: 70 cu. ft. heating chamber: 12 retorts; the Belgian standard for direct-fired furnace is usually given as 1 sq. ft. grate area: 18 cu. ft. heating chamber: 6 retorts.¹

The furnace is fired by the coking method, *i.e.*, coal fills the inclined charging door, Fig. 136, and is piled up outside on a plate resting on brackets (not shown). When the coal on the grate has lost most of its volatile matter and the caked residue has been partly burned, the coal in the charging door is pushed down and spread, and fresh coal fed.

In the roof of a chamber are two flues, Fig. 133, 9 in. square, 3 ft. from the end walls; the flues from two adjoining chambers end in the chimney 11 by 27 in.

The inclined retorts vary in size, ranging from 3 ft. 6 in. to 4 ft. in length and from $7\frac{1}{2}$ to $8\frac{1}{2}$ ft. in diameter, the retort with large diameter holds the more refractory charge in the hotter part of the furnace.

In front of the furnace is the residuum pit, 6 in. wide, which delivers the refuse from the retorts into the ash pit.

In our days direct-fired furnaces are the exception, as most zinc smelteries are large establishments in which the advantages of gas-firing have made direct-firing obsolete; the coal consumption in the latter case is $2\frac{1}{2}$ to 4 tons per ton of ore, depending upon the character of the fuel (see Table 34).

90. Hegeler Furnace, Producer Gas, Waste-heat Boiler.—The characteristic is a double rectangular furnace, 90 to 125 ft. long, about 12 ft. wide and 11 ft. high with gas producer close to one end which furnishes the heating gas needed, Figs. 139 and 140; the hot gas travels horizontally through the furnace, is burned gradually by air blast which enters in regulated amounts through tiers of tuyere pipes placed in the sides at such intervals as to enclose four retorts of a row. In the early eighties the hot waste gas passed off into the open, at present it enters a brick chamber leading to vertical waste-heat boilers. These are² of standard design as the draft requirements are low, because the furnaces are operated with slight pressure. The temperature of the entering gas is about 1,000°. The earlier Hegeler furnace erected in 1872 at La Salle, Ill.,³ was different from the later form, in that it was relatively small, that

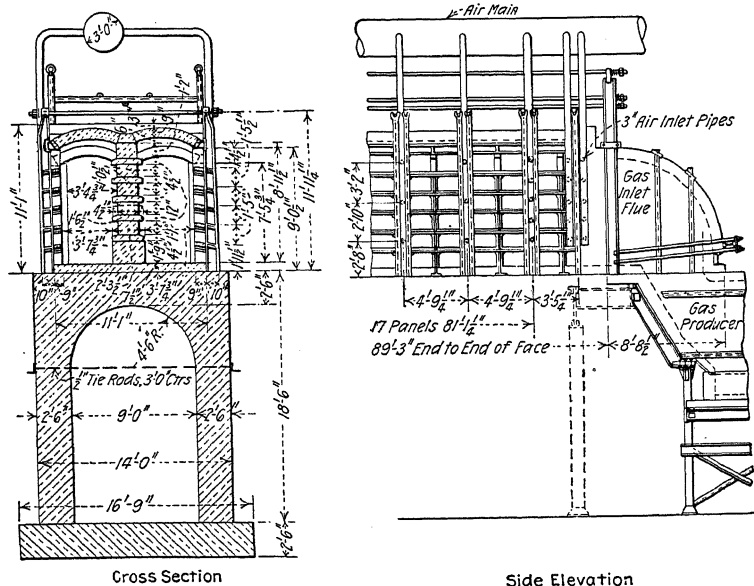
¹ See also Laur, *Bull. VInd. Min.*, 1874, III, 395.

² Pratt, *Chem. Met. Eng.*, 1917, XVI, 30.

³ *Berg. Hüttenm. Z.*, 1875, XXXIV, 173, ill.; *Min. Res. U. S.*, 1882, p. 378.

the producer gas was burned in a chamber above the retorts, and the flame drawn downward between the retorts into ports connected with flue and chimney.

The Hegeler furnace of the Mineral Point Zinc Co., Depue, Ill., and gas producer are shown in Figs. 139 to 142. The furnace, Figs. 139 to 140, is 89 ft. 3 in. long, 12 ft. 9 in. wide, and 11 ft. 1 in. high. It rests upon the walls of a tunnel in which terminate the chutes (not shown) receiving the retort residues at the working

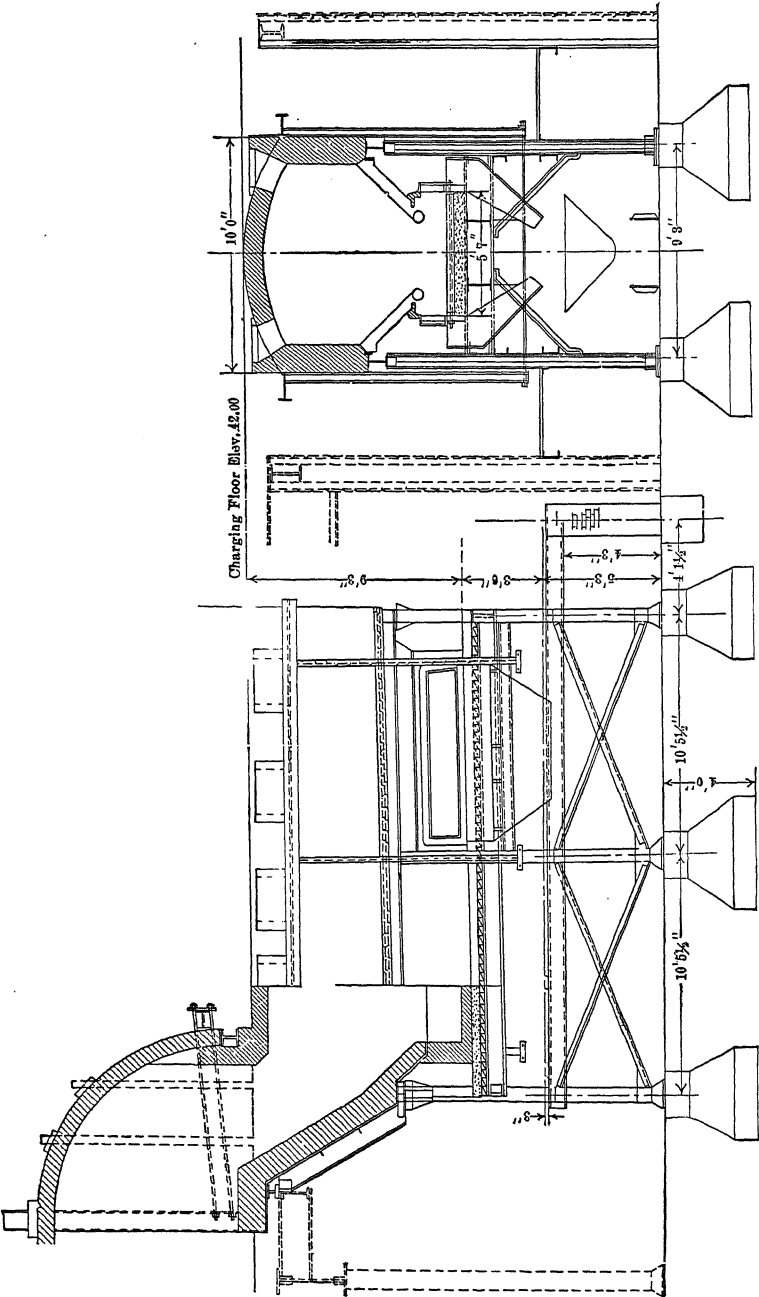


FIGS. 139 and 140.—Hegeler furnace, Mineral Point Zinc Co., Depue, Ill.

faces. The furnace has the usual stanchions on the sides tied by rods, and at the ends heavy steel buck stays also tied by rods. The roofs of the chambers rest on skew backs let into the upper parts of the stanchions and on the center pillar. The furnace has 15 full-size sections or panels, 4 ft. $9\frac{1}{4}$ in. wide, and two small-size, 3 ft. $5\frac{1}{4}$ in. wide, at the ends. The full-size panels have 10 niches each with its pair of retorts, the small size have half the number or five. There are five tiers of retorts, making a total of 320 retorts on a side, or 640 in all. The retorts are circular, have an inner diameter of $8\frac{5}{8}$ in. and an inner length of $54\frac{1}{4}$ in., the cubic content is 1.62 cu. ft.

The inlet flue for producer gas, at one end of the furnace, is provided with a damper to regulate the flow of gas. The air main, 3 ft. in diameter, runs longitudinally over the top of the furnace; it has 6-in. branches provided with dampers descending along the stanchions, each branch has five 3-in. air-inlet pipes provided with gates. The air inlets into the furnace are larger than 3 in. and are reduced in size by inserting an iron rod. At the entrance of the gas-inlet flue is a pair of 6-in. branches; the space in the furnace is left clear of the retorts in order that the gas may become well mixed with the first supply of air and the larger part burned in the first section. The hot waste gas from section 1 heats section 2; as the temperature thus obtained is not sufficiently high, part of the remaining producer gas is burned by the second tier of air pipes; the same process is repeated in the third, fourth and remaining sections. The temperature near the gas inlet is the highest and falls gradually toward the outlet. In the cooler part of the furnace are charged oxide, skimmings and other materials easy of reduction. The air is supplied by a Sturtevant blower, with discharge 25 by 28 in., which delivers per minute 666 cu. ft. air into the main at the pressure of $1\frac{1}{2}$ in. water. The waste gases pass from the outlet into two 300-hp. Babcock and Wilcox waste-heat boilers. There is provided a stack to carry off the gases when the boiler is to be cleaned or repaired. Boiler tubes need to be blown daily. The even distribution of flame in the hot compartments is accomplished by gates in the outlets. In order to see at a glance whether the distribution is correct, there is placed on either side in the top row of retorts at the entrance of the flame a clay cylinder, or rather a retort without bottom, with condenser attached. Lengths of flames issuing from the two condensers indicate whether one side receives more gas than the other. In addition to gates in the outlets, some furnaces have at the inlet a wall with ports which can be partly closed by sliding tiles.

Three to four Hegeler producers, shown in Figs. 141 and 142, furnish the gas necessary for a furnace. A producer has an oblong sloping firebrick chamber, 16 ft. long, 7 ft. 8 in. wide and 3 ft. 4 in. high, carried by I-beams; the sides of the chamber end in tile boshes which rest on a water-cooled frame and terminate in heavy cast-iron air pipes; the bottom, 5 ft. 7 in. wide, is closed by cast-iron plates. Beneath the water-cooled frames are hinged cleaning doors through which ashes and clinkers are discharged into chutes delivering into cars. The roof has four charging-doors on a side. The air, warmed during its passage through longitudinal cast-iron pipes,



Figs. 141 and 142.—Hegeler gas producer.

enters two blow-boxes incorporated in the ash bottom, and passes from these through the ash bed into the producer. Being operated without steam, the producer makes heavy clinkers which have to be removed every $1\frac{1}{2}$ or 2 hr. The producer gasifies 36 tons of coal in 24 hr.

This Hegeler producer first used at La Salle and other Illinois smelteries is being replaced by more modern types, such as the Duff, Chapman, Hughes, Swindell, Wood, Morgan.¹ Some plants have one large producer to a furnace; others prefer to have two smaller size, as in case of accident or when repairs are needed, one producer can be cut out temporarily and the work of the other forced.

The latest Hegeler furnace is the one of the American Steel & Wire Co. at Donora, Pa. It is 120 ft. long, 11 ft. $4\frac{1}{2}$ in. wide and 9 ft. 10 in. high, has six rows of retorts 8 in. inside diameter and 52 in. long, 19 sections each with 24 retorts or 456 retorts on a side, or 912 in all. Producer gas is furnished by two 10-ft. Hughes producers each of which gasifies 2,000 lb. coal per hour; the waste gases pass through a Rust boiler of 588 hp. and then into a concrete stack 5 ft. 6 in. in diameter and 125 ft. high (see Table 34).

A recent improvement in the Hegeler type of furnace is the one by Ziesing² who introduced wing walls between each section of retorts which extend outward to near the front of the furnace. They cause the producer gas to burn near the front, and the flame to eddy back in the several sections, with the result that the retorts are more uniformly heated. The furnaces at Grasselli, Ind., have been rebuilt with wing walls.

The principle of the Hegeler furnace has found much favor, but in recent years experience has shown that its coal consumption was greater than that of the Siemens-Belgian or Neureuther type. Thus³ of the furnaces at Roselake and Hillsboro owned by the same company, the Siemens furnace requires per ton of oxide ore 1 ton coal for smelting and $\frac{1}{2}$ ton for power, or $1\frac{1}{2}$ tons in all; while the Hegeler requires $2\frac{1}{2}$ tons.

91. Convers & DeSaulles Furnace, Producer Gas, Recuperator.—At the works of the New Jersey Zinc Co. at Bethlehem, Pa., distilling furnaces with recuperator and regenerator systems of heat recovery were run parallel for a considerable time. An outcome of the work was the development of the Convers & DeSaulles recuperator fur-

¹ Brooks-Nitchie, *Tr. A. I. M. E.*, 1920, LXIII, 846.

² Ingalls, *Eng. Min. J.*, 1919, CVII, 87.

³ Ingalls, *Eng. Min. J.*, 1919, CVII, 87.



SECTION C-D

FIGS. 143 and 144.—Convers-De Saulles furnace.

SECTION A-B

nace.¹ Since 1902 some of the details have been changed. The furnace in operation at Palmerton, Pa., is shown by vertical cross and longitudinal sections in Figs. 143 and 144. The furnace, 35 ft. 4 in. long by 17 ft. 6 in. wide, is 10 ft. 10½ in. high above the working floor and extends 24 ft. 8 in. beneath it. It is a double furnace with five rows of oval retorts, 26 in a row, or 130 on a side.² A retort is 57 in. long inside, 9 in. high, 7 in. wide, and has a volume of 1.62 cu. ft. A charge is made up of 78 lb. ore (48 per cent Zn) and 28 lb. fuel. The furnace is fired with producer gas generated in a Hughes producer, 8 ft. 6 in. in diameter and 7 ft. high, which gasifies 12 tons buckwheat anthracite in 24 hr. The gas enters two mains, 3 ft. 1½ in. wide and 1 ft. ½ in. high to the spring of arch sprung on a radius of 3 ft. 9½ in.; the mains are placed between the recuperators, the heating chambers and the waste products flue, and heat the gas which leaves the gas main through 13 ports, 6 in. square, and enters the combustion chamber alternating with similar air ports. The air enters the furnace through two air inlets beneath the recuperators; the air from one inlet ascends in the recuperator through 17 flues, 5¼ by 12¾ in., is heated to 600°C., passes into the hot-air chamber from which 14 flues, 6 in. square, alternating with the gas ports deliver into the combustion chamber. Pre-heated gas and air, delivered 4 ft. above the bottoms of the two combustion chambers, furnish two sheets of flame which ascend in the combustion chambers, heat the retorts, are deflected by the roof, and descend together in a waste-products flue, 8 in. wide, and pass through the 13 ports, 11½ by 20 in., into the waste-products main, 6 ft. 1 in. by 1 ft. 8 in. Here they are divided into two streams; which make three passes through two recuperators having nine horizontal flues, 4¾ by 9¼ in., and enter the main flue leading to the stack; they arrive in the upper flue on the right side of Fig. 144 and leave by the lower flue on the left side; the temperature is reduced to 600°C. The end walls of the waste-products flues in the recuperators have pigeon-hole walls to permit blowing out the horizontal flues.

A combustion chamber is 8 ft. 9¼ in. high at the front wall, and 9 ft. 7½ in. at the center of the arch; it is 2 ft. 11½ in. wide and 26 ft. long; its volume is 689 cu. ft. The surface of the waste-heat flues of a recuperator is 2,915 sq. ft., and the volume of the brickwork 470 cu. ft. The heating fuel consumed is 3,000 lb. buckwheat

¹ U. S. Patent No. 712,502, Nov. 4, 1902.

² The latest furnace has six rows of retorts, 20 in a row, or 120 on a side.

anthracite to 2,000 lb. ore with 58 per cent Zn, or $1\frac{1}{2}$ tons of coal to 1 ton of ore, often it is only 1.3 tons. The furnace produces 7,100 lb. spelter per day, requires 1.03 man hours per ton of ore, or 2.49 man hours per ton of spelter. The life of a retort approximates 27 days (see Table 34).

92. Neureuther-Siemens Furnace, Producer Gas, Regenerator.—

The Siemens regenerator system of utilizing waste heat from zinc distilling furnaces for pre-heating furnace gas and air came into use between 1860 and 1870.¹ The general arrangement used at first is shown in Fig. 145. Gas and air enter the regenerator chambers

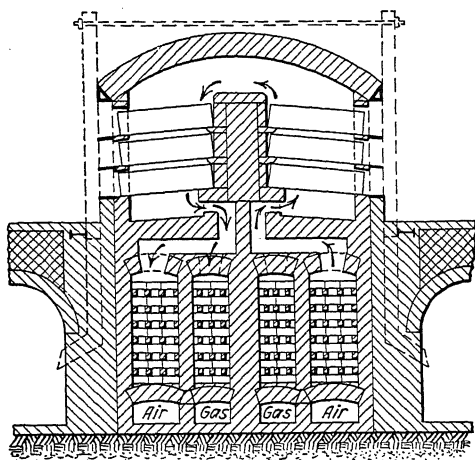


FIG. 145.—Siemens furnace.

to the right, rise and are heated; upon leaving, pre-heated gas is burned by pre-heated air, and the flame rises in one of the chambers, heats the retorts, strikes the roof and is deflected; it then descends in the other half of the chamber, heats the retorts, passes downward to the other pair of regenerator chambers, gives up its heat, and enters ports leading to the horizontal flues connected by reversing valves with the stack. On reversing the valves every 25 to 30 min., the travel of gas and air, of flame, and of waste gas is in a direction opposite that shown by the arrows. The disadvantages encountered at first were, that a furnace was not heated uniformly, the temperature was too high where gas and air met, and too low where the waste gas left the chamber, and that the checkers became clogged

¹ *Berg. Hüttenm. Z.*, 1869, XXVIII, 405.

with oxides. The difficulty of overheating the bottom retorts has been overcome by the Neureuther three-port furnace in operation at the works of the Illinois Zinc Co., Peru, Ill.¹ The furnace is 100 ft. long, has five rows of retorts 54 in. long; the gas is furnished by Swindell producers.²

A furnace of similar construction which is in operation at the works of the Mineral Point Zinc Co., Depue, Ill., is shown by vertical cross and longitudinal sections in Figs. 146 and 147, and by

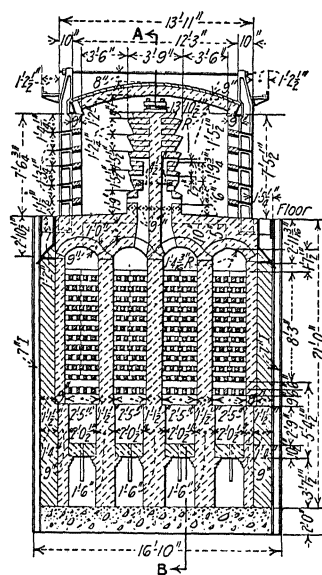


FIG. 146.

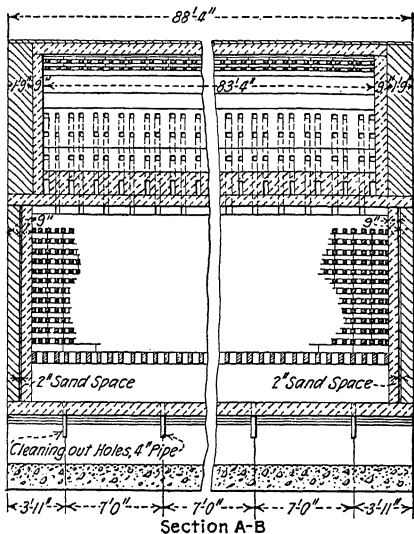


FIG. 147.

FIGS. 146-150.—Neureuther-Siemens furnace, Mineral Point Zinc Co., Depue, Ill.

details of gas and air ports and of retorts in Figs. 148 to 150. The furnace, Figs. 146 and 147, 88 ft. 4 in. long and 13 ft. 11 in. wide, is 9 ft. 4½ in. high from the working floor to the top of the roof; the regenerators, of the same length as the furnace but 16 ft. 4½ in. wide extend downward 21 ft. from the floor. The furnace has five rows of retorts, 400 on a side or 800 in all, which are placed in the usual way. The two lower rows, Fig. 148, have an outer diameter

¹ U. S. Patent No. 666,390, Jan. 22, 1901.

Litigation over Siemens zinc distillation furnace, *Eng. Min. J.*, 1910, LXXXIX, 654.

² *Min. Ind.*, 1907, XVI, 929.

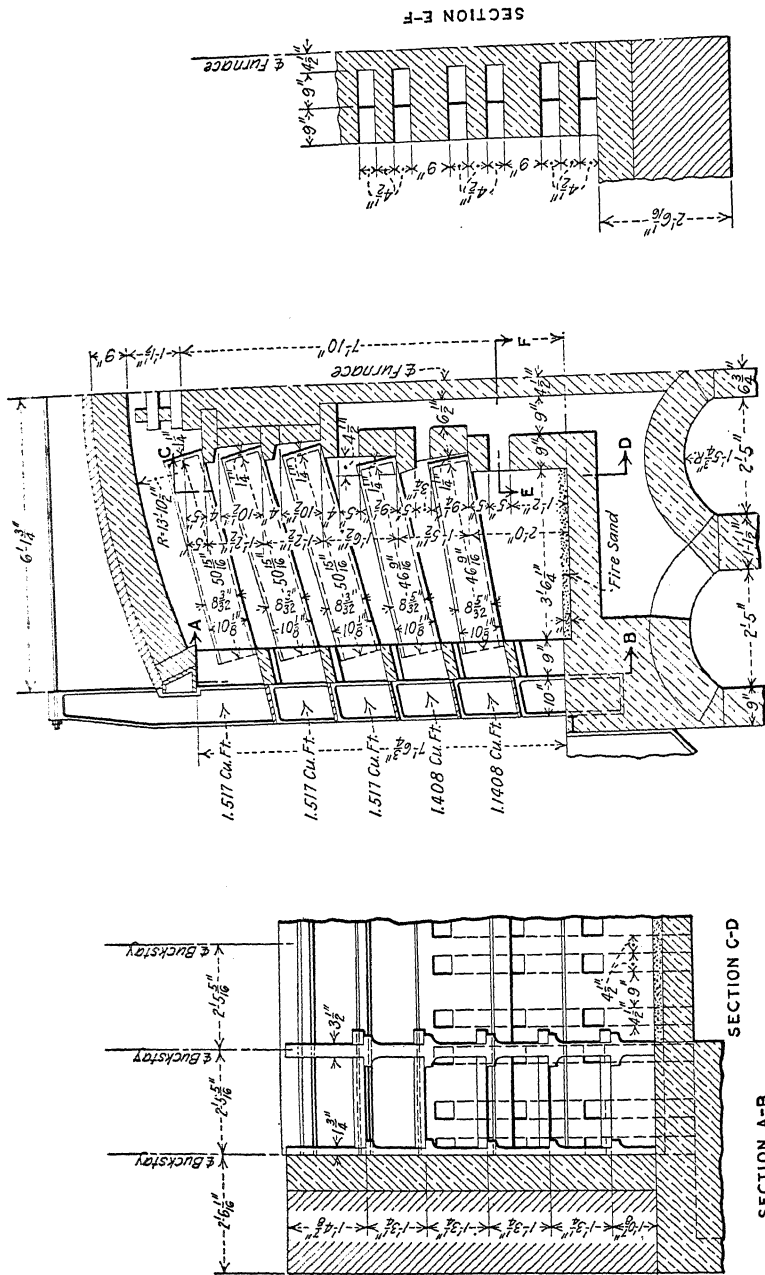


FIG. 148.

FIG. 149.

FIG. 150.

of $10\frac{1}{8}$ in. and an inner of $8\frac{5}{8}$ in.; the outer length is $48\frac{1}{16}$ in. and the inner $46\frac{9}{16}$ in., the three upper rows have an outer diameter of $10\frac{1}{8}$ in. and an inner of $8\frac{3}{8}$, the outer length is $51\frac{9}{16}$ in. and the inner $50\frac{5}{16}$ in. The total retort capacity is 1,119 cu. ft. A combustion chamber, 3 ft. 6 in. wide, 7 ft. $6\frac{3}{4}$ in. high, and 83 ft. 4 in. long has a capacity of 2,206 cu. ft. The inner gas and outer air regenerators are of the same size, they are 11 ft. $9\frac{1}{2}$ in. high, 2 ft. 5 in. wide, and 85 ft. 4 in. long; the space occupied by the checkers is 9 ft. 3 in. high, 2 ft. 5 in. wide, and 85 ft. 4 in. long, which represents a capacity of 3,814 cu. ft. for one pair. The 400 retorts on one side represent a volume of 939 cu. ft., the combustion chamber one of 2,206 cu. ft., and the checkers of one pair of regenerators a space of 3,814 cu. ft.; or 1 cu. ft. of retort space has 2.35 cu. ft. of combustion chamber, and 4.06 cu. ft. of checker work. On the bottom of the furnace is a chamber, 83 ft. 4 in. long and 2 ft. wide, to receive dust discharged from the 4-in. clean-out pipes. Above the chamber are the two entrance flues for gas and air, 2 ft. $\frac{1}{2}$ in. wide, gas and air rise through a distributing grate and enter the checkers. Heated to 800°C ., they meet, Figs. 146 and 149, at right angles; the flame rises in the back flue, 9 in. wide at the bottom and contracted to 6 in. higher up, and enters the combustion chamber through three tiers of flues 9 and $4\frac{1}{2}$ in. apart, Fig. 148, which enclose the two lower rows of retorts, Fig. 149.

The producer gas is furnished by a modified Duff producer with Chapman agitator¹ 10 ft. in diameter which gasifies 10 to 12 tons of coal in 24 hr. The coal consumption is 0.8 ton per ton of roasted ore (see Table 34).

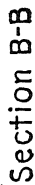
H. & J. W. Hegeler² have gone one step farther than Neureuther. They introduce³ all the air necessary under the bottom row of retorts through a series of ports, and admit gas at the back between the retorts; thus a furnace with six rows of retorts has one row of air ports and six rows of gas ports.

93. Furnace Fired with Natural Gas.—The furnaces fired with natural gas are very much alike. In Figs. 151 and 152 are given vertical cross and longitudinal sections of a furnace operated by the Prime Western Spelter Co. at Tulsa, Okla. It is a double furnace with 680 retorts in five rows, 340 on a side. The general arrangement of retorts is the one common to most furnaces. The

¹ Brooks-Nitchie, *Tr. A. I. M. E.*, 1920, LXIII, 857.

² U. S. Patent No. 792,773, June 30, 1905.

³ *Electrochem. Ind.*, 1905, III, 276.



FIGS. 151 and 152.—Belgian furnace, natural gas.

use of natural gas at a pressure from 8 to 12 oz. greatly simplifies the construction. At one end is the gas main, 4 in. in diameter, from which a branch of the same diameter, resting on brackets, extends along either side of the length of the furnace. From a branch, gas-feed pipes, $1\frac{1}{2}$ in. in diameter and provided with dampers, pass downward, 28 to 29 in. apart near the entrance and twice the distance farther on; a feed pipe has four gated delivery tuyeres which enter the combustion chamber above the bottom and below the top row of retorts, and deliver gas at a pressure of from 8 to 12 oz. The air, delivered by a blower at about the same pressure, arrives in the main, 24 in. in diameter, running over the furnace along the central line. From it branches extend downward, each having four tuyere pipes disposed as shown in Fig. 152. Gas and air usually enter the furnace through special brick blocks. The principle of firing followed is that of the Hegeler furnace, given in §90. The waste gases leave the furnace at the end through a flue, 1 ft. 6 in. by 2 ft. 6 in., which ends in a stack 37 ft. in height (see Table 34).

In a number of plants the single long combustion chamber with stack at one end has been divided in two by a central partition wall, and a chimney placed at either end. This appears to give better control of operations and to simplify repairs.

At the works of the Edgar Zinc Co., Cherryvale, Kan., the original double furnace with 200 retorts, 100 to a side in five rows of 20 each, has been divided into two parts, each having a chimney to carry off the waste gases. The method of firing has also been changed. At each end is an underground passage with a 3-in. gas main; from this branches off one set of pipes which furnishes gas to the end burners, and another set which furnishes gas to the front burners. The gas from the end burners is ignited in a combustion chamber from which the flame enters the distillation chamber beneath the bottom and at the second row of retorts. The gas from the front burners enters the distillation chamber near the stanchions beneath the third row of pipes. The gas is at a pressure of 8 to 12 oz. and draws in the necessary air through air nipples.

C. A. H. DeSaulles¹ has applied a principle of admitting producer gas and air in the Convers-DeSaulles furnace to a furnace fired with natural gas.

94. **Wettengel and Other Furnaces.**²—The Wettengel is a rotatable

¹ U. S. Patent No. 1,041,977, Oct. 22, 1912; *Met. Chem. Eng.*, 1912, x, 816.

² *Electrochem. Met. Ind.*, 1908, vi, 457; *Eng. Min. J.*, 1911, xci, 670.

furnace which does away with charging and discharging by hand. It consists of a horizontal steel shell with two rows of retorts which is supported on wheels and rotated by means of a worm gear. The interior is lined with tiles and shelves for the support of the retorts. Burners are placed in the back, in the bottom and at the top. Above the furnace is a charging bin with hoppers, each large enough to hold the charge of one retort and provided with a shut-off slide and a telescopic spout to be lowered into the retort. Below the furnace are hoppers to receive the residue. When the retorts have been filled, the furnace is turned over that the retorts may be in position for distillation; the condensers are inserted, loamed, stuffed, and vented. When the distillation is finished, the zinc and blue powder are collected, the condensers removed, and the furnace rotated to discharge the residue. The furnace now is turned up to bring the retorts in a horizontal position that they may be cleaned; it is then turned in the opposite direction through an angle of 270 deg. that the retorts may receive their charges and when turned for a further 90 deg. be ready for distillation. The bottom of the retort now forms the top, and any adhering slag will drip down on to the charge and will be removed with the residue at the next discharge. This method almost entirely avoids scraping of retorts, retards slag perforation, utilizes both sides, keeps the retort straight, and more than doubles their lives. In treating Joplin ore with 4 to 5 per cent Fe the usual life of a retort of 30 days was lengthened to 154 days. The objection to the furnace is that the mechanism is expensive and that the recovery of zinc is about the same as in the ordinary furnace.

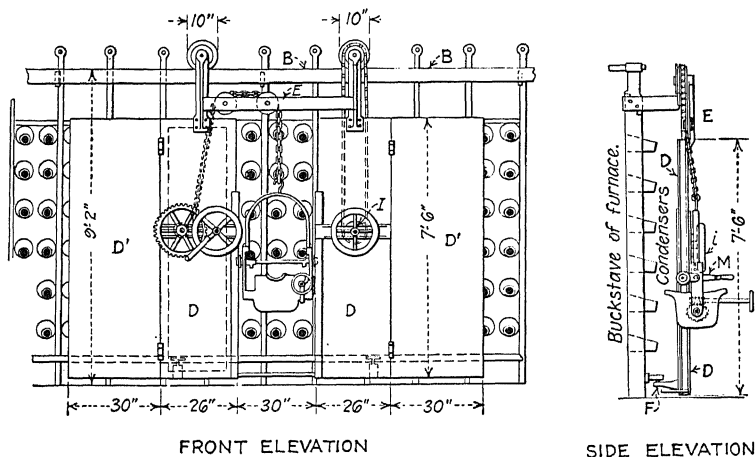
The Hughes Furnace.¹—A retort is held in place in an inclined rotary shell or combustion chamber. Ore charge fed continuously at the upper end passes through the retort, zinc vapor and residue are collected at the lower end in a condenser. A retort 8 in. in diameter and 6 ft. long is expected to treat in 24 hr. 25 tons of ore.

The Thum Furnace.²—The late F. A. Thum constructed a gas-fired furnace with five rows of retorts for treating lead-bearing zinc ores. The retorts, or rather tubes, were steeply inclined and open at both ends; to the upper end was attached a condenser, to the lower a tile with tap hole well luted. The lead collecting at the lower end was tapped, and the residue raked out. The charge was introduced from the lower end. The furnace is not in use.

¹ *Min. World*, 1909, XXI, 131.

² *Berg. Hüttenm. Z.*, 1875, XXXIV, 1.

95. **Accessory Apparatus and Tools.**—The heat radiating from the front of a furnace interferes with the operations, such as charging, discharging, etc., of retorts. In order to protect the men, there are used with small furnaces multiple folding sheet-iron shutters hinged to the stanchions, by means of which the lower, central, or upper condensers can be covered severally or together; the shutters when unfolded are far enough away from the furnace to permit discharging the residues into the cinder pockets. Above them are suspended pieces of corrugated iron to serve as a protection against heat.



FIGS. 153 and 154.—Chapman shield.

At Scailgneaux, Belgium¹ there is suspended a short distance from the front a curtain made of hollow wedge-shaped pivoted slats which have openings for the circulation of air.

In modern large furnaces the stationary shutters have been replaced by balanced sheet-iron curtains suspended from a traveling trolley. In addition, there is provided a crane on a four-wheeled truck for holding a suspended pot into which is drawn molten metal from the retorts. The crane has been replaced in many instances by a vertical shield attached to a car. The Chapman shield² shown in front and side elevations in Figs. 153 and 154 is a typical device. It consists of two pairs of hinged sheet-iron plates *D D'*

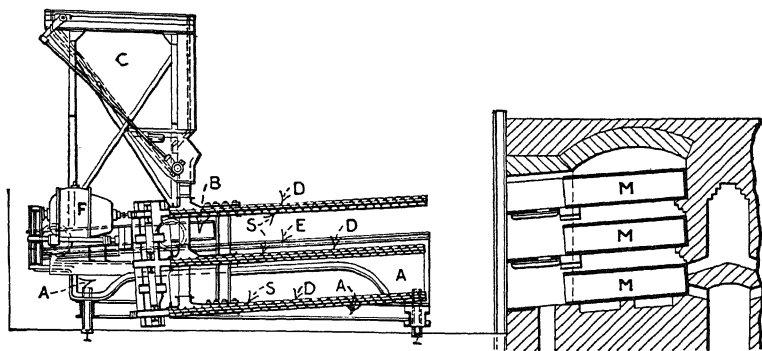
¹ *Eng. Min. J.*, 1913, xcvi, 790.

² *Min. Ind.*, 1900, ix, 680.

stiffened by angle iron and held 30 in. apart at top and bottom by crosspieces *E* and *F*. Plates *D* have near the tops hangers by means of which the shield is suspended from trolleys traveling on a track supported by brackets bolted to the buck stays; near the bottom they have brackets carrying rollers which bear against the guide rail bolted to the lower ends of the buck stays. In this way the shield is kept vertical and can be moved readily to and fro by means of hand- and sprocket-wheels on shaft *I* connected by chain with sprocket- and groove-wheels on the upper rail. Between plates *D* is suspended by trunnions and hangers a tilting ladle which can be raised and lowered in guides by a windlass; a lever *M'*, pivoted on the hangers, allows thrusting outward the ladle to avoid the condensers; a worm gear effects the tilting.

FIG. 155.—Charge scoop.

For charging the retorts, the ore mixture arrives in one- or two-story charge cars with gates at the ends from which the contents are removed with a charging scoop and thrown into the retorts.



FIGS. 156 and 157.—Saeger charging machine.

Such a scoop is shown in Fig. 155, it has a handle 4 ft. long and a trough 18 in. long, 5 in. wide and $2\frac{1}{2}$ in. deep. Hand-charging is the common method of procedure. It is hard, slow and unhealthy work, which requires considerable skill.

In recent years mechanical charging has made some headway. The Saeger charging machine shown in cross-section in Figs. 156 and 157 is one of the first successful apparatus. Its leading parts are the lower truck *A*, the upper truck *B*, the charge hopper *C*, and the conveyor troughs *S*. Truck *A* is an iron frame running along

the front of the furnace which has a platform for the motorman and carries the frame of truck *B*; the latter can be moved forward and backward on rails *E* by cog-wheel gearing connected with the motor *F*. The motor also runs the screw conveyors *S* in covered steel troughs by means of cog-wheel bearings. The flow of charge from *C* through feed pipes into conveyors is regulated. In operating, the motorman brings machine in front of a set of retorts, moves forward truck *B* until the conveyor troughs *D* enter the mouth of the retorts, and starts the screw conveyors; while these are feeding, truck *B* continues to move forward until the screw conveyors have reached the ends of the retorts filling them part full, truck *B* is then thrown out of gear and runs backward automatically, while the conveyors continue to feed until they leave the retorts. The machine shown is intended to serve a Rhenish furnace which has three superposed niches each with two retorts, it therefore has six conveyor troughs, arranged in three pairs to serve three stories. At Rosdzin, Silesia, the 120 retorts on one side of a furnace are charged in 20 min., or one retort in 10 sec. At the works of the National Zinc Co., Bartlesville, Okla., hand-charging of the furnace¹ takes 3 hr., while a Saeger machine did it in 1 hr. and charged 2,000 lb. more than can be done by hand. Two difficulties have been encountered with feeding flotation concentrates, as these are likely to clog the augers, and the charges, being packed tightly are likely to be blown out. The feeders have therefore been discarded.

The Dor-Delattre machine² in use in Belgium, has the form of a motor-driven centrifugal fan, with feed hopper on one side of the casing, hinged peripheral discharge tube and a propeller with radial blades. It has been tried in this country, but has not been adopted. Mechanical charging will probably replace hand charging in the future; the various devices tried so far have not been successful.

In discharging retorts, zinc is raked out from the condenser by means of a rabble into a suspended ladle; the rabble has a head about $1\frac{1}{2}$ in. in diameter and a handle $2\frac{1}{2}$ ft. long. The condensers are then removed and scraped, and the residue from the retort discharged. The residue used to be and is still largely raked out by long- and short-handled rabbles, about 8 and 4 ft. long, with heads 3 by 4 in.; crust and slags are removed with chisel pointed bars (spießes) usually 8 ft. long. About 1885 R. Lanyon started at Pittsburg, Kan., blowing out with steam the ashes from the retorts,

¹ *Min. Ind.*, 1914, XXIII, 96.

² *Eng. Min. J.*, 1909, LXXXVII, 1,272; 1910, XC, 73.

a mode of operating which has become very common. An iron shield, provided with openings corresponding to a set of retorts, is suspended in front of the furnace, a 1-in. wrought-iron pipe about 8 ft. long connected with wired hose to a main is inserted, thrust to the back of the retort, and then steam turned on; the ashes are blown out against the shield and drop into the residue pocket on the floor. The apparatus devised by Lanyon had at the end of the pipe a

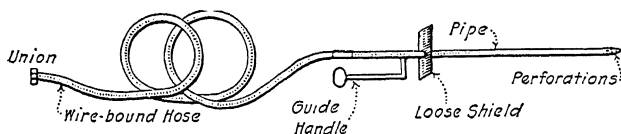


FIG. 158.—Blow-out holes and pipe.

conical shield with slot.¹ Water has taken the place of steam in most plants. A blow-out hose and pipe are shown in Fig. 158. A vacuum-cleaning device has been constructed by Heinz.²

The discharging of retorts by hand, even with the use of steam or a jet of water, is an arduous piece of work, hence mechanical dischargers have come into play. The Saeger cleaning machine,³ Fig. 159, resembles in its general features the inventor's charging machine, Figs. 156 and 157. It has a lower truck *A* moving along

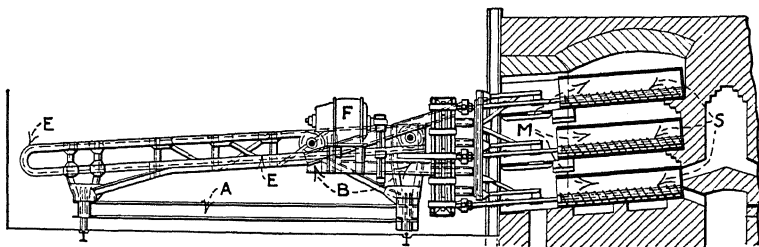


FIG. 159.—Saeger cleaning machine.

the front of the furnace, guide rails *E* on which the upper truck *B* is moved forward and backward by motor *F*, and screw conveyors *S* with troughs; truck *A* carries the platform for the motorman. The conveyors having been brought to the mouths of the retorts are set in motion, and begin to discharge the retorts; truck *B* is moved forward until the conveyors have reached the backs of the retorts

¹ Clerc, *Eng. Min. J.*, 1885, XXXIX, 441.

² *Mel. Chem. Eng.*, 1916, XIV, 103.

³ *Metallurgie*, 1910, VII, 39; *Eng. Min. J.*, 1910, LXXXIX, 780.

and is then returned to its first position. In order to keep the conveyors cool a spray of water is admitted. In a furnace with 120 retorts on a side, a retort is discharged in 15 sec.

*The Simmonds Discharging Machine.*¹—This machine was introduced at Iola, Kan., in 1914, and is found in several plants. As seen in the patent drawing, Fig. 160, it consists of a truck carrying a series of movable bars, each with a sprocket wheel at the ends over

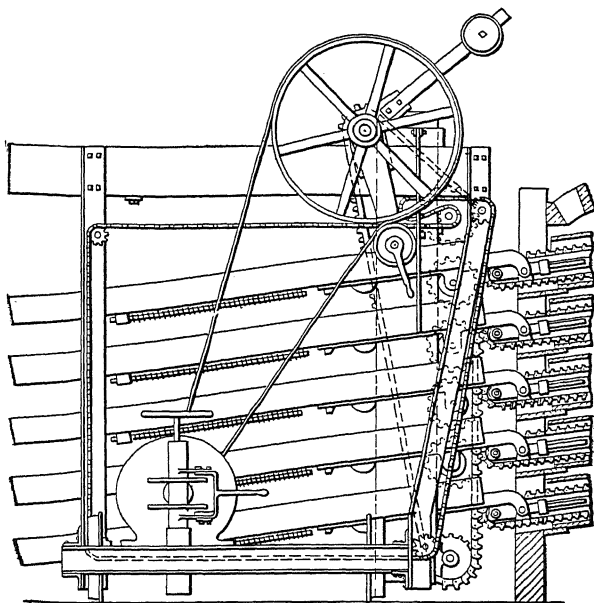


FIG. 160.—Simmonds discharging machine.

which travels an endless chain with cast-steel scrapers. The machine is run up facing a tier of retorts, the scrapers are introduced, set in motion, and travel to the end of the retort, raking out the residue. When one tier has been cleaned, the scrapers are returned to the starting point, the truck is moved ahead, and another tier of retorts cleaned. It takes about 45 sec. to clean a tier of retorts, *i.e.*, 5 sec. to move the scrapers to the mouths of the retorts, 25 sec. to discharge the tier, 10 sec. to withdraw the scrapers, and 5 sec. to move the truck to the next tier.

96. Starting of Furnace.—In starting a new direct-fired furnace, two methods have to be considered. One is to bring the empty

¹ *Met. Chem. Eng.*, 1914, XII, 789; *Min. Ind.*, 1914, XXIII, 797; *Eng. Min. J.*, 1915, XCIX, 449.

chamber gradually to a red heat, and then to put in place the retorts taken red hot from the baking oven; the other is to put in place in the cold furnace the dried retorts, and start with the firing. The latter method is the one common at present. The niches holding the dried retorts are closed with old retorts, bricks, or tiles instead of the usual clay mixture, because the use of wet clay disintegrates the mouth of a retort that has not been baked. A fire is started in the charged furnace and kept going for about 2 days in order to dry off the moisture and to bring the furnace and the retorts to a red heat; the third day the fire is urged; the fourth day the retorts are charged with a readily reducible oxide mixed with an excess of reducing fuel over normal, and the condensers inserted. The oxide will be reduced, but no zinc, or only a very small amount will be obtained. The fifth day the heat is increased, and charges, made up of oxide and a smaller excess of reducing fuel, smelted. This procedure continues until in 8 days after starting, normal heat has been reached and normal charges are worked. Retorts made with hydraulic presses do normal work in 5 to 6 days.

In replacing a defective retort in a working furnace by a hot one from the baking oven, it takes 2 days or more before the retort furnishes its normal amount of zinc. This is due to the porosity of the retort walls, which allow zinc vapor to pass out and furnace gases to enter, and to the absorption metal.

In starting a gas-fired furnace, special precautions have to be taken to avoid explosions. The retorts are put in place and the niches closed; one or more parts of the furnace are left empty to leave room for temporary fireplaces from which the furnace is brought in about 5 days to the kindling temperature producer gas, that is 600° to 700°C.; at this temperature the soot which had settled on the walls will have been burned off. Some gas is now turned on, the flue leading from the producer to the furnace having been warmed by a wood fire so that the gas shall not be cooled. The temporary fireplaces are removed and their spaces filled with hot retorts from the baking oven. These operations cause the furnace to cool somewhat; it is then brought to the required temperature by increasing the volume of producer gas; light charges are introduced which are made heavier as in the direct-fired furnace. At some plants the fireplaces are heated with cord wood for about a week; then the three upper rows are filled with baked retorts, firing with gas is begun, and the other retorts are introduced from the baking oven, a row at a time.

In starting a gas-fired furnace with regenerative chambers, care has to be taken to heat the retort chamber as well as the regenerators. The chambers are filled with retorts with the exception of spaces reserved for temporary fireplaces. First wood and then coal fires are started, and the valves reversed every half hour. In 4 or 5 days the furnace chambers will be dull red, and in 2 days more hot enough to ignite producer gas. The gas is now turned on in small amounts at first, the fireplaces are removed, red-hot retorts put in their places, and the temperature raised by increasing the volume of gas.

97. Regular Work; Discharging and Charging.—The operation is based on the time required to treat a charge which is 24 hr. The day shift, arriving at 3:00, 4:00 or 5:00 a.m., finds the distillation of the charges finished, the last drawings of metal accomplished, and the temperature somewhat low. The first step is the removal of the prolongs and the condensers from the top row. A suspended, balanced

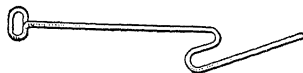


FIG. 161.—Tool for handling condenser.

sheet-iron curtain, wide enough to cover three rows of retorts, is lowered, and a platform suspended from trolleys raised, so that the top row of retorts is laid bare, and the helper mounting the platform is protected from the heat of the furnace. He removes the condensers from the top row by means of a tool shown in Fig. 161, hands them to an assistant on the furnace floor who receives them with a similar tool and places them upright on the floor. The next step is to remove the residue in the mouth of the retort which is always rich in zinc and is re-treated. The finished charge is now raked or blown out, by means of tools or apparatus discussed in §94, into the residue pocket which runs along the front of the furnace. Defective retorts are replaced by new ones taken red hot from the baking oven. The empty retorts are charged either by hand with a scoop or by a machine as outlined in §94. Charging by hand requires skill to avoid spilling, and force to pack the charge; from seven to nine scoopfuls are required for a retort. In the small hand-fired furnaces the retorts are charged by rows, one man on the floor shoveling the mixture onto the platform, and the other scooping it into the retort. The retorts are thus filled from the top down. In large furnaces the work on the retorts is done in tiers by three crews, the one removing the condensers is followed by a second clearing out the retorts, and this by a third filling the empty retorts. In the meantime a helper empties the contents of the prolongs into boxes and scrapes clean the condensers with the scratcher button,

Fig. 162. When a retort has been filled it is "spießed," *i.e.*, a small iron rod is inserted toward the top of the charge to furnish an opening for vapors and gas to escape, and prevent the charge from being blown out. The condensers are now put in place with a holder, Fig. 163, and closed in part with a stuffing mixture of non-caking coal and clay. With a small hand-fired furnace holding 60 retorts, emptying and recharging takes three men $3\frac{1}{2}$ hr. With a large furnace, 240 retorts are cleaned and charged in 4 hr. by six men, usually from 4:00 to 8:00 a.m., several crews attack the work at the same time.

Mechanical discharging and charging a retort by means of the Saeger machine takes 25 sec.

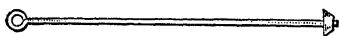


FIG. 162.—Scratcher button.

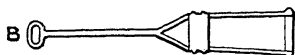


FIG. 163.—Condenser holder.

98. Distillation.—The heat in the furnace which had fallen somewhat during the preceding operation is increased to bring the temperature to normal. Even before the last retorts have been charged, vapors of water and hydrocarbons are set free from the retorts that were filled first; the hydrocarbons are ignited, burn with a luminous flame which becomes lighter as the hydrocarbons diminish and carbon monoxide increases, later the purplish carbon-monoxide flame becomes bluish-green from zinc vapor which burns with a whitish smoke. The smoke becomes brownish in the presence of cadmium. When smoke appears, the prolongs are slipped over the condensers. At first, the zinc that comes over is mixed with blue powder owing to the small amount of zinc vapor present, to the chilling of zinc vapor by condenser being too cool, or to the presence of carbon dioxide; later comparatively little blue powder will be formed as zinc vapor is set free in large amounts and the condenser has attained the correct temperature of 415° to 550°C. , and as carbon dioxide is present only in very small amounts. Care is had to keep the condenser at its proper heat.

The zinc is removed from the condenser three times in 24 hr., or three draws are made, into a suspended movable kettle, covered with charcoal or coke dust, which is swung under the condensers. The first zinc is removed at 2:00 p.m., the second at 10:00 p.m., and the third at 3:00 a.m. When a kettlefull of metal has been collected, the dross is skimmed, and the spelter poured into ingot

molds, 9 by 18 by $1\frac{1}{4}$ to $1\frac{3}{8}$ in., which furnish slabs weighing 52 to 57 lb. Table 30¹ gives three examples of the proportional amounts of zinc obtained in three and four draws.

TABLE 30.—AMOUNTS OF SPELTER IN THREE AND FOUR DRAWS

Draw	Charge	Blue powder	Total
Smelting $\frac{1}{2}$ Western Sulphide, $\frac{1}{2}$ Leadville Calamine			
1	27.0 per cent	15.1 per cent	37.8 per cent
2	36.5 per cent	18.6 per cent	55.1 per cent
3	0.6 per cent	6.5 per cent	7.1 per cent
	—	—	—
	67.8 per cent	32.2 per cent	100.0 per cent
Smelting $\frac{2}{3}$ Joplin Sulphide, $\frac{1}{3}$ Leadville Calamine			
1	27.6 per cent	10.2 per cent	37.8 per cent
2	35.2 per cent	15.0 per cent	50.2 per cent
3	5.0 per cent	7.0 per cent	12.0 per cent
	—	—	—
	68.1 per cent	31.9 per cent	100.0 per cent
Smelting Joplin Sulphide			
1		20 per cent *	
2		32 per cent †	
3		39 per cent †	
4		9 per cent †	
		—	
		100 per cent	

* Two top and two bottom rows.

† Whole furnace.

The metal first drawn is purest having been distilled at a comparatively low temperature, the second is less pure than the first, and the third less than the second. Thus Wemple² gives in Table 31 figures showing the distribution of impurities from three draws made in distilling ore and blue-powder charges.

The metal first drawn from an ore charge is lowest in Pb and Fe and higher in Cd, and the blue-powder metal is higher in Pb and Fe, and lower in Cd than the ore metal. Another example is given by Johnson.³

¹ Johnson, *Inst. Chem. Eng.*, 1918, XVIII, 135.

² *Tr. A. I. M. E.*, 1918, LIX, 173.

³ *Loc. cit.*

TABLE 31.—IMPURITIES IN METAL OF THREE DRAWS FROM ORE AND BLUE-POWDER CHARGES

Draw	Product	Pb, per cent	Fe, per cent	Cd, per cent
1	Ore.....	0.58	0.019	0.460
	Blue powder.....	0.82	0.039	0.330
2	Ore.....	1.05	0.038	0.138
	Blue powder.....	1.48	0.068	0.074
3	Ore and blue powder.....	1.84	0.121	0.030

The temperature maintained in distillation is high, it increases from the time of charging to that of discharging the retorts; it is raised more quickly to the desired degree when blende rich in Fe forms the charge (§74) than when low. Temperature measurements of retorts and furnace (probably the Hegeler gas-fired furnace at La Salle) during the 24 hr. of working a charge made by Mühlhaeuser¹ are given in Table 32. The temperatures are degrees centigrade, the letters *R* and *F* mean retort and furnace. The first measurement at 11:00 a.m. was made after the removal of the condenser, the second at 11:30 after withdrawal of the residue, the third after introduction of the charge, and the last at 12:45 a.m. next day after withdrawal of the residue. Leaving out slight irregularities, the temperature is lowest, 1,067°, after charging, and highest, at the end of distillation, 1,309°; the difference in temperature between the inside of retort and of furnace at first is large, 300°, decreases slowly at first but more quickly later on until constant difference of about 100° is attained.

Johnson² has summarized his temperature measurements with Norton-Seger cones on furnaces treating Joplin ore with Zn 54.6, Fe 4.2, SiO₂ 6.1, Pb 0.76 per cent; they are given in Table 33.

The data show the gradual increase of temperature in retort and furnace, also that a furnace attains the given temperature more quickly than its retorts; a direct comparison of the working of the four types of furnaces cannot well be made except that in the direct-fired furnace the rise in temperature is slower than in the gas-fired Hegeler furnace.

Another set of data by the author³ shows the changes of temperature in the checker work of a regenerative furnace due to the reversal of valves.

¹ *Zt. angew. Chem.*, XVI, 278.

² *Mct. Chem. Eng.*, 1917, XVII, 302.

³ *Mct. Chem. Eng.*, 1918, XVIII, 14.

TABLE 33.—TEMPERATURE MEASUREMENTS OF RETORTS AND FURNACES

Furnace	Measure- ment in	Temperatures attained								Charging a.m.	
		Time								Start	End
		1,090°C.	1,130°C.	1,170°C.	1,210°C.	1,250°C.	1,270°C.	1,290°C.	1,310°C.		
Natural gas....	Retort	1:20	2:57	5:10	7:55	9:48	12:00	1:10		4:00	9:00
Regenerative....	Retort	12:40	1:50	3:45	5:40	7:55	10:30	1:15	3:20	5:00	11:00
Hegeler.....	Furnace	11:55	1:03	5:00	8:00	10:20	12:20	5:00		5:00	10:00
Coal-fired.....	Furnace	11:00	12:00	2:00	4:00	6:00	8:00	10:00	12:00	5:00	10:00

RHENISH METHOD OF DISTILLATION

99. Introductory.—This method of working, also called Belgo-Silesian, is a modification of the Belgian developed in the Westphalian and Rhenish provinces of Prussia. It is used largely on the European continent, but is represented in the United States only at Pueblo, Colo. It differs from the Belgian method in that it has three tiers of inclined oval retorts supported at the ends instead of the usual six cylindrical retorts of the latter; this makes the Rhenish furnace lower than the Belgian. The charges are distilled in 24 hr. The requirements to be fulfilled for successful work are the same in both methods.

The forms of retorts and condensers have been given in §79.

The furnaces formerly were fired direct; at present all furnaces are heated with producer gas; in a few instances mentioned below illuminating gas has come into use. Two types may serve as illustrations, one without heat recovery from the waste gases, the other with recovery by means of Siemens regenerators; the latter has become almost characteristic with Rhenish furnaces.

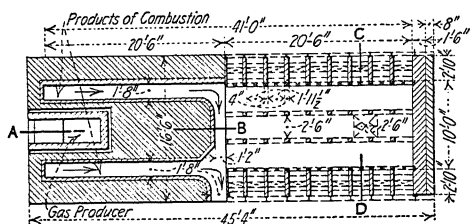
100. Furnaces. (a) *Furnace Gas-fired without Heat Recovery.*—Such a furnace described by E. F. Dürre¹ is shown in Figs. 164 to 166. It occupies a floor space 45 ft. 4 in. by 15 ft. 8 in., the height from furnace floor to top is 10 ft. 4 in., the depth to bottom of ashpit 10 ft. The furnace has 216 elliptical retorts, 108 on a side in three rows of 36. At each end is a Boëtius gas producer with grate 38 by 50 in., that is the air to burn the producer gas is heated in flues surrounding the producer. The two grates represent a grate area of 26.4 sq. ft.; the combustion chamber 10 ft. wide, 41 ft. long, and 6 ft. 2 in. high, has a volume of 2,829 cu. ft.; the ratio is 1 : 1,088. The flame from the producer rises along the central line of the furnace, heats the back ends of the retorts, is deflected by the roof, descends at the front ends of the retorts, and passes through a flue on either side of the producer; the two flues unite in a main conduit of 14 sq. ft. in a section. Three hoods on a side carry off gases and vapors. Some facts of a similar furnace in operation at Dortmund, Westphalia, are given by Association des Ingénieurs.²

(b) *Original Overpelt Furnace, Gas-fired with Siemens Regenerators.*—The characteristic of the Overpelt furnace is that it consists of

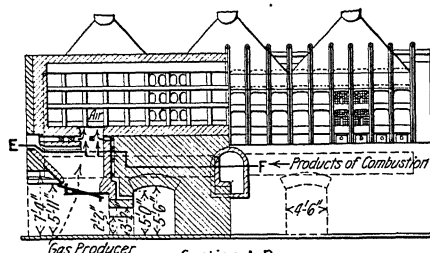
¹ "Ziele und Grenzen der Electrometallurgie," Leipsic, 1896, p. 207, through Ingalls, W. R., "Metallurgy of Zinc and Cadmium," McGraw-Hill Book Co., Inc., N. Y., 1903, p. 417.

² *Rev. Univ. Mines*, 1894, xxv, 38.

two blocks, separated by an open space for the manipulation of gas and air valves. Each block is filled with the same number of retorts and provided with a pair of regenerators. While block No. 1 preheats in its regenerators gas and air which are burned around the retorts, block No. 2 receives from block No. 1 the products of combustion which heat the retorts, and conducts them through ports into regenerators which deliver into the stack. Every half hour gas and air currents are reversed, so that in the present in-



Section E-F
FIG. 164



Section A-B
FIG. 165

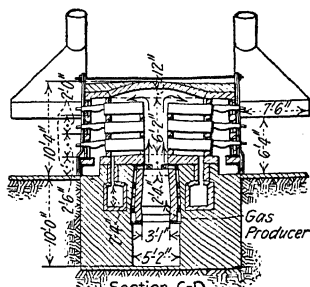


FIG.166

FIGS. 164, 165 and 166.—Rhenish furnace, gas fired, non-recuperative.

stance block No. 2 receives gas and air, while block No. 1 takes products of combustion from block No. 2 and delivers them to the stack.

Two vertical cross-sections of a block are given in Fig. 167. The furnace has 240 oval retorts, 120 on a side arranged in three rows of 40 each. As there are two connected blocks, each will have half the number of retorts. The retorts, 49 to 51 in. long, $10\frac{1}{4}$ to 12 in. high and 7 in. wide, rest with the closed ends on the broken back wall, and the front ends in the niches on tiles ending in cast-iron plates. The plates have openings for the discharge of retort residues which are closed by sliding doors. The residues are collected in iron hoppers with swing doors. A retort receives the charge of 90 to 110 lb. ore with about 45 per cent of reducing fuel,

and is worked in 24 hr. The condenser is similar to the one given in Fig. 119; it remains in place while the spelter is being removed and a fresh charge introduced. The residues are removed through a separate opening in the front of the retort.

In Fig. 167 air or producer gas are delivered to the regenerators, take up the heat stored, meet in the central flue, and burn. The flame passes outward through the side ports at the top, and travels the length of the block; it then enters the other block, travels

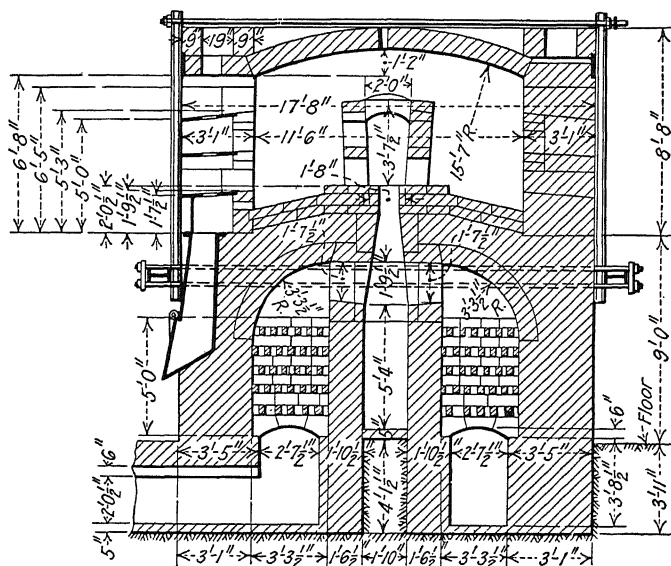


FIG. 167.—Original Overpelt furnace, gas-fired, recuperative.

through the combustion chamber, leaves this through the top and the broken side wall of the central flue, and enters the two regenerators, when, having dropped its heat in the checker work, it will enter the bottom flues which end in a main leading to the reversing valves and thence to the stack.

While the coal consumption in this furnace is low, about .1 ton of coal to 1 ton of ore, the main disadvantage has been the short life of the central flue which melted away quickly. Hence construction of the original furnace has undergone a number of changes. One of these is represented by the furnace of the United States Zinc Co., at Pueblo, Colo.

(c) *Colorado Overpelt Furnace*.—Figures 168 and 169 give a horizontal section, showing the passage of gas, air and products of combustion through regenerators and valve to stack, and a vertical cross-section showing the passage through regenerators and furnace. The furnace resembles in its general features the original Overpelt. It is 58 ft. 5 in. long, 17 ft. 8 in. wide, 8 ft. 2½ in. above the floor, and has a cellar 13 ft. 7½ in. deep. It is made up of two blocks each with three rows of oval retorts, 22 to a row, or 66 to a side, which is equivalent to 132 to the block, or 264 to the furnace. In Fig. 168 the passages of gas, air, and products of combustion are indicated by arrows. The gas is furnished by three producers (Duff 6 by 6 ft., Morgan 10 ft., Hughes 10 ft., not shown) which deliver it into a header. A branch leads to the stack, while the main line conducts the gas to a gas valve. From this the gas travels as indicated through a flue to one regenerator of a block. The air is delivered from a blower to the butterfly valve and travels, as shown by arrows, to the other regenerator of the same block. Gas and air ascend in the regenerators, shown in Fig. 169, are pre-heated to about 700°C., and meet. The flame is divided, each branch rises on its side of the central wall and passes off into its combustion chamber through two rows of ports, 5 in. high and 4½ in. wide, one beneath the bottom the other beneath the top row of retorts. The combined flames sweep through the combustion chambers of the other block, heat the retorts, enter the two rows of ports on either side of the central wall, descend in two vertical flues, traverse the regenerators, pass through horizontal flues to the butterfly and gas valves, unite, and are delivered to a conduit leading to the stack. The valves are reversed every 30 min. The oval retorts, made of Colorado clays, are 64 in. long, 6 in. wide, and 12 in. high. A retort holds a charge of 250 lb. roasted blende with 42 to 44 per cent zinc and 60 per cent coal. The fuel consumption is 0.9 ton coal per ton of roasted ore. The yield in spelter is 85 per cent, which is high considering the Fe-content of the blende, and is rendered possible by the reduction of Fe_2O_3 with coal in the Hegeler furnace referred to in §74 (see Table 34).

(d) *Ferraris Furnace*.—At the Monteponi works¹ there are in operation furnaces with Siemens regenerative chambers heated with the excess gas of 4,500 Cal. obtained from a by-product coking plant. A furnace has 216 oval retorts, 61.4 in. long and 7.874 by 11.81 in. in section. The air is heated to 700°C. in the regenerators,

¹ Ferraris, *Eng. Min. J.*, 1918, CVI, 212; drawing.

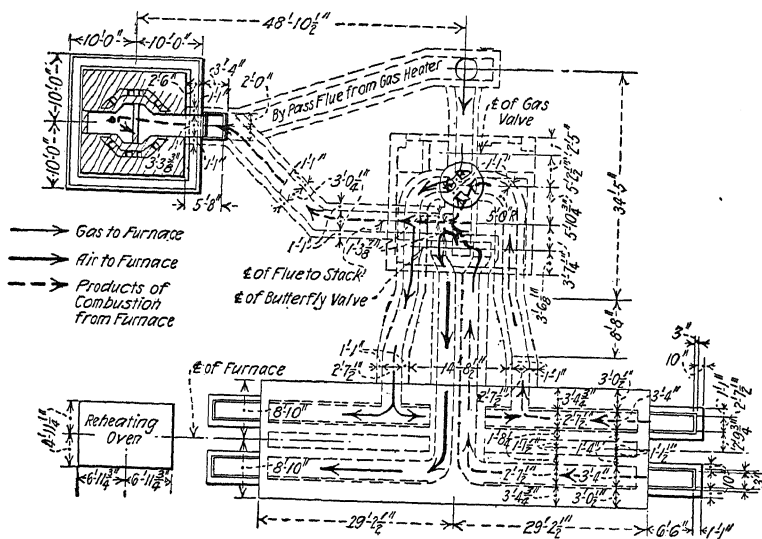


FIG. 168.

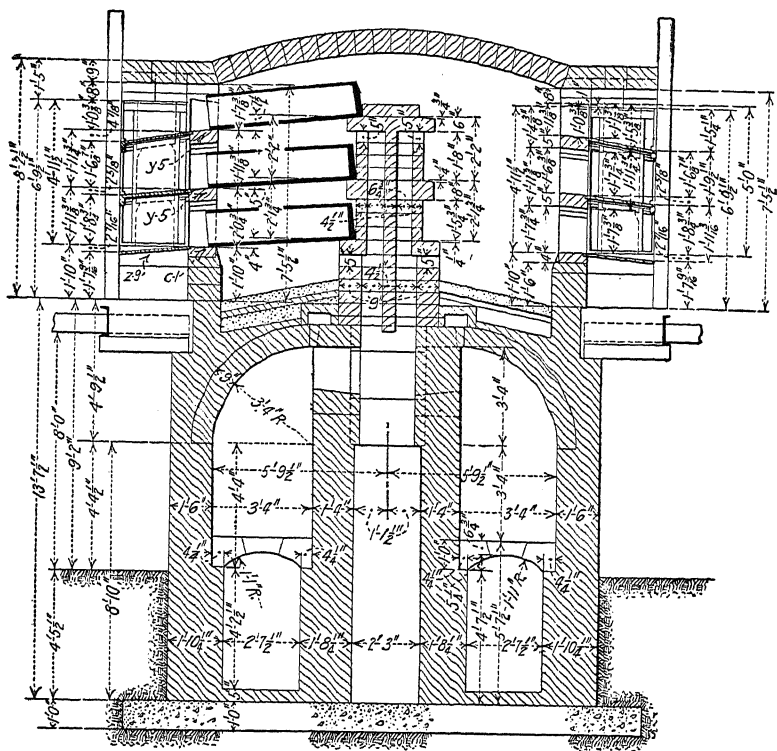


FIG. 169.

FIGS. 168 and 169.—Colorado Overpelt furnace, gas-fired, recuperative.

the valves being reversed every 30 min. The furnace charge is crushed to 0.1181 in., a retort holds 71 lb. of ore which are distilled in the usual 24 hr. The daily gas consumption is 282,525 cu. ft. in smelting ores easy of reduction, and less than 353,156 cu. ft. with difficult ores. About 44 cu. ft. gas are required for 1 net ton of ore.

Singmaster¹ states that at Hamborn, Germany, coke oven gas is used in roasting blende and distilling the roasted ore in Rhenish furnaces. The Monteponi plant appears to have been the first to use coke oven gas as the fuel for distilling ores.

(e) *The Ruck Furnace*² at the Crown Spelter works is a three-high Rhenish furnace with Siemens regenerators. Some of the gas and air conduits are placed in the front wall in order to improve the heating of the front ends of the retort which usually are less hot than the rear. The coal consumption is 1.15 tons per ton of ore containing 46.54 per cent Zn. This is an improvement over the results obtained with the earlier furnaces.

SILESIAN METHOD OF DISTILLATION

101. Introductory.—The characteristic of this method of working is the use of a single row of large size muffles resting with their bases on the bed of the furnace. The muffles are in contact with the flame only at the back, front and sides are heated by radiation. The condensers of a pair of muffles are held in a niche. The single furnaces with four muffles and without stack, in use at the beginning of the nineteenth century, were replaced about 1810 by double furnaces with 10 or more muffles on a side; all furnaces at present are double. Furnaces were at first direct-fired,³ since about 1870 they are gas-fired.⁴ The two methods of gas-firing without and with Siemens regenerators are in operation at present. The ores used at first in Silesia were carbonates, easy of reduction; this permitted the use of large muffles and low temperatures. With the advent of blende, the ores became more refractory; mixtures containing e.g., 62 per cent roasted blende and 32 per cent calcined carbonate required higher temperatures. Ores of lower grade can be treated better in the large muffle than in the small retort. The

¹ *Eng. Min. J.*, 1918, CVI, 537.

² *Eng. Min. J.*, 1919, XVII, 307.

³ Klemann, L., "Die Zinkgewinnung in Oberschlesien," Kern, Breslau, 1860, 43 pp., 3 plates.

⁴ Georgi, *Berg. Hüttenm. Z.*, 1877, XXXVI, 78.



4

4

³ Föhr, *Berg. Hüttenm. Z.*, 1883, XLII, 4, 13.

into the bottom one, what remains is raked out every second or third day. A form differing slightly from the above is given by Spirek.¹

The furnace is heated from two producers with step grates. The gas ascends in the inclined flue *k*, enters the upper part of the shaft *Z* where it meets pre-heated air at *b*, which is delivered by a fan into the horizontal air main *C*, and ascends in branch flues *V*. The flame passes along the backs of the muffles, is deflected by the roof to either side and heats the tops and sides of the muffle. The waste gas is drawn to the ends of the combustion chamber, enters through flues *n* the ovens *T*, intended for baking muffles, and furnaces *G*, intended for calcining ores, and then passes off through flues *f* into the stack. The waste gas not required for baking and calcining leaves the furnaces through low chimneys *e*. The lower part of shaft *Z* is a dust chamber which is entered by ports *m* from passage *R*. At the front the lower parts of the niches are closed by clay tiles placed against the partition walls; the upper parts are closed by sheet-iron doors having stoking

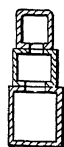


FIG. 172

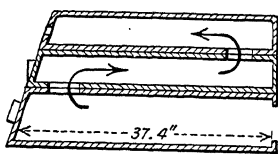


FIG. 173

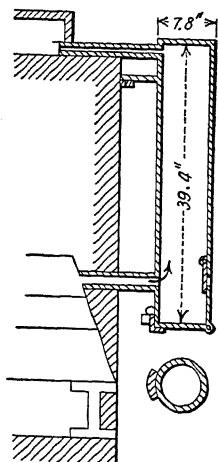


FIG. 174

Figs. 172, 173 and 174.—Dagner condenser and prolong.

and peep holes. Beneath the mouths of a pair of muffles is the flue *g* into which is raked the slag; it is covered with a tile except at the backs of the partition walls *o*. Chutes *n* lead to the cinder pockets which also carry off some fume.² The fumes from the prolongs pass off through flues. The charges are introduced through the condenser with a long-handled scoop. A charged muffle is three-quarters filled, the charge slanting from back to front.

¹ *Oest. Zt. Berg. Hüttenw.*, 1881, XXIX, 352, Plate x, Figs. 18 to 20.

² *Schmieder, Berg. Hüttenm. Z.*, 1890, XLIX, 301.

Distillation lasts 16 to 18 hr., the rest of the 24 hr. is taken up with charging and discharging. A 24-hr. charge consists of 2.3 tons ore made up of roasted blende (42 to 45 per cent Zn), calcined carbonate lump ore (25 to 32 per cent Zn), 0.15 ton raw carbonate ore (14 to 16 per cent Zn), and 1.3 tons reducing fuel (51 per cent). The charge yields 850 lb. crude spelter which corresponds to a recovery of 80 per cent. Ten men tend a furnace in 24 hr. The coal consumption is 3.35 tons run of mine, or 6.83 lb. per pound of crude spelter.

Regenerative.—No drawings of modern furnaces with Siemens regenerative chambers appear to have been published; only the older types have found their way into print.¹ The general arrangement of the leading parts of a modern furnace, as given by Spirek,² is shown in Figs. 175 and 176. The furnace has two pairs of regenerative chambers for gas G' and for air L' , each with its bottom flues g and l . Gas from the producer and air from the fan arrive in g and l , rise in one pair of regenerators, are heated, travel to the end of the furnace, enter the combustion chamber through flues J and burn. The flame travels over the backs of the muffles to the opposite end of the chamber, leaves through ports J of the second pair of regenerators, descends in them to the bottom flues, and passes through reversing valves into the stack. On reversing the valves, gas and air rise in the second pair of regenerators, are heated, travel to the opposite end of the furnace, enter there the combustion chamber through ports J , when the flame after heating the retort, descends in the first pair of regenerators, drops its heat, leaves through bottom flues, enters the reversing valves and the stack. The principle of heating the muffles is therefore similar to that of the Overpelt furnace. The muffles are not shown; b are cast-iron Cochlovius frames³ which replace the usual tiles forming the sides of the niches; a are chutes leading into the under ground passage R ; S is a dust chamber.

Georgi⁴ comparing the work of two Silesian smelteries using regenerative furnaces with 56 muffles, and non-regenerative with 24 muffles, finds the following: The regenerative furnace treated in 24 hr. 5,414 kg. ore, burned 8,100 kg. coal (1.45 per cent on the ore),

¹ *Berg. Hüttenm. Z.*, 1867, XXVI, 362; 1869, XXVIII, 405; 1870, XXIX, 92; 1877, XXXVI, 80.

² *Oest. Zt. Berg. Hüttenw.*, 1881, XXXIX, 336.

³ *Dingl. Polytech. J.*, 1880, CCXXXVII, 301.

⁴ *Berg. Hüttenm. Z.*, 1877, XXXVI, 80.

needed 1.42 muffles and yielded per ton of ore 11.39 per cent zinc; the cost per 100 kg. crude spelter was 32.34 M. The non-regenerative furnace treated 1,757 kg. ore, burned 4,610 kg. coal (2.62 per cent on the ore), needed 1.75 muffles, and yielded per ton of ore 11.17 per cent zinc; the cost per 100 kg. crude spelter was 36.20 M.

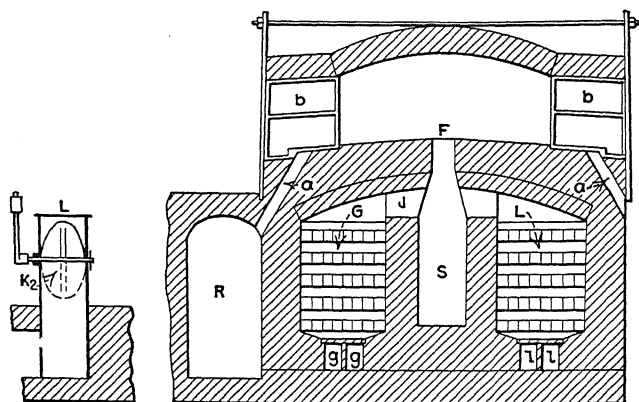


FIG. 175

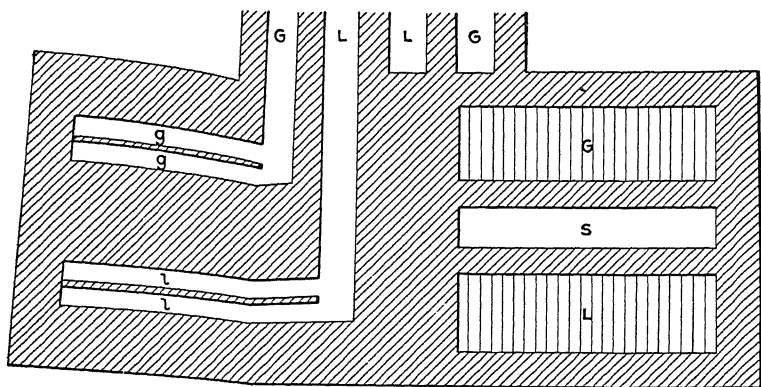


FIG. 176

FIGS. 175 and 176.—Silesian furnace, regenerative.

More favorable results are given by Schnabel-Louis¹ in a comparison of a regenerative furnace with 60, and a non-regenerative furnace with 32 muffles. The regenerative furnace treated in 24 hr. 6 tons ore, burned per ton of ore 1.016 tons of coal, needed 1 muffle

¹ "Handbook of Metallurgy," 1907, II, p. 202.

for 5 tons of ore, and extracted 13 per cent zinc per ton of ore; the corresponding figures for the regenerative furnace were 3 tons of ore, 1.33 tons of coal, 1.6 retorts, 13 per cent zinc.

OTHER METHODS OF DISTILLATION

103. Introductory.—The methods of working discussed in §§88 to 102 are the three standards by which practically all zinc ores are distilled. Two methods of historical interest may be noted, the English and the Carinthian; modifications of the latter have been recently developed by Binon and Grandfils and by Roitzheim and Remy; the Steger furnace forms a class by itself.

104. The English Method.—The characteristic of this method,¹ which has become obsolete but was in operation in England in 1859, is the use of a large pot with cover as a reducing vessel; the pot has an opening in the bottom through which the zinc vapor passes and is conducted by means of a tube into a condensing chamber beneath. The distillation takes place *per descensum* instead of *per ascensum* as is the case in all other methods. The first zinc works of England erected at Bristol² used this method of distillation, which appears³ to be an adaptation of the ancient Indian or Chinese mode of operating.

105. The Carinthian Method.—The characteristic of this method is the use of small vertical retorts closed at the tops and ending in tubes leading into a single condensation chamber. The tubes, in operation at Delach, Carinthia, in 1824,⁴ were 39.37 in. long, 4.48 in. in diameter at top and 3.23 in. at bottom; they received charges of 5.5 to 6.6 lb. of ore; the tops were filled for a distance of 3.93 in. with reducing fuel.

Another form of vertical retort is the one by Binon and Grandfils⁵ shown in Fig. 177, in which *A* is the retort, 7 ft. 10½ in. long and 1 ft. 3¾ in. in diameter, *a* the supporting elbow with plate *d* having a tap-hole for lead, *e* cover, *f* condenser, *h* supporting tiles. From 12 to 16 retorts were held in a heating chamber. The retort is not in operation.

¹ Percy, J., "Metallurgy," Murray, London, 1861, p. 550.

² Beckman-Johnston, "History of Inventions," p. 344, quoted on p. 3.

³ Hommel, *Eng. Min. J.*, 1912, XCIII, 1185.

⁴ Percy, J.-Knapp, F., "Die Metallurgie," Vieweg, Brunswick, 1863, p. 50.

⁵ Rev. Univ. Mines, 1877, v, 228; Pamphlet, "Étude sur l'amélioration des Procédés de Fabrication du Zinc," Vaillant-Carmanne, Liège, 1878; *Berg. Hüttenm. Z.*, 1880, XXXIX, 10; *Oest. Zt. Berg. Hüttenw.*, 1881, XXIX, 325.

The use of vertical retorts has recently been revived in the Roitzheim-Remy Furnace¹ in which vertical cylinders are charged mechanically at the top and discharged in the same manner at the bottom. The ore at the top and the residue at the bottom prevent air from entering. The retorts have horizontal condensers. Details are not available as yet, their work is praised highly by the author.

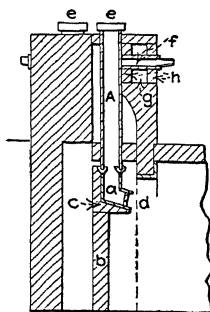


FIG. 177.—Vertical retort, Bignon and Grandfils.

Steger Basic Built-up Retorts.—In 1894 Steger,² constructed a distillation furnace with three rows of arched horizontal retorts alternating with heating flues. The retorts were built of magnesite brick. The advantages claimed for this material in comparison with fireclay, were greater heat conductivity and strength, and smaller fusibility, corrodibility and absorption of zinc. The idea does not appear to have met the exigencies of practice.

FURNACE TABLE, RESULTS, PRODUCTS

106. Introductory.—In §§88 to 105 have been discussed some typical furnaces in use in the United States for distillation of zinc ores. Bringing together in a table the leading facts of the furnaces considered and the results obtained gives an insight which cannot be arrived at as readily in another way. The products resulting from the distillation are very much the same whatever may have been the furnace used. There exists, however, a variety of methods for converting intermediary into finished products, and these will be discussed with some detail.

107. Furnace Table.—A table giving facts about furnaces in Europe and the United States was published by Borchers in 1908.³

Of the furnaces discussed the Belgian direct-fired has become obsolete in the United States. The Hegeler furnace is very much in evidence, but has probably seen its best days as fuel consumption is high. There are cheaper ways of raising steam than by the waste heat of a distilling furnace. The Convers-De Saulles furnace is in operation only at the Palmerton works of the New Jersey

¹ Liebig, *Metall u. Erz.*, 1916, XIII, 143, 177.

² *Zt. B. H. u. S. W. i. Pr.*, 1894, XLII, 163.

³ *Metallurgie*, 1908, v, 522.

TABLE 34.—DISTILLATION FURNACES

Items	Belgian, direct-fired, Joplin, Mo.	Hegeler, Donora, Pa.	Convers- De Saulles, Palmerton, Pa.	Neureuther, Depue, Ill.	Belgian, natural gas, Tulsa, Okla.	Colorado Overpeck, Pueblo, Colo.
Retort, length, inches inside.....	46	54 $\frac{1}{2}$	57	46 $\frac{1}{2}$ and 50 $\frac{1}{2}$	50	64
width, inches inside.....	7 $\frac{1}{2}$	8 $\frac{1}{2}$	7	8 $\frac{3}{4}$ and 8 $\frac{3}{8}$	8 $\frac{1}{4}$ and 8 $\frac{1}{8}$	6
height, inches inside.....	7 $\frac{1}{2}$	8 $\frac{1}{2}$	9	8 $\frac{3}{4}$ and 8 $\frac{3}{8}$	8 $\frac{1}{4}$ and 8 $\frac{1}{8}$	12
volume, cubic feet inside.....	0.88	1.02	1.04	1.40 and 1.49	1.547 and 1.018	2.35
ore, pounds; zinc, per cent.....	44; 55	71.31; 68.18	78; 48	52; 62	61; 50	250; 42-44
reducing fuel, pounds.....	22	39.27	38	34	33 $\frac{1}{2}$	150
life, days.....	25	50-60	26	20	37	25-26
number in a row.....	14	76	24	80	68	40
number of rows.....	7	6	5	5	5	3
number on a side.....	98	456	120	400	340	120
Heating fuel.....						
solid; pounds per ton ore.....	6,000					
grate; length by width, feet						
ftches.....						
producer gas; coal, pounds per ton						
ore.....	two, 8.0 by 0.5					
producer, kind.....						
natural gas; cubic feet per ton ore.						
pressure.....						
Combustion chamber on one side,						
cubic feet.....	550	314.5	689	2,206	2,017	1,834
length by width by height, feet	15.5 by 4.0 by	7 ft. 6 in. by 4 ft.	26 ft. by 2 ft. 11 $\frac{1}{2}$	13 ft. 4 in. by 3 ft.	69 ft. 7 $\frac{1}{2}$ in. by	54 ft. 7 in. by 4
inches.....	9.0	11 $\frac{1}{2}$ in. by 8 ft.	in. by 9 ft. 7 $\frac{1}{2}$	6 in. by 7 ft. 6 $\frac{1}{2}$	3 ft. 10 $\frac{1}{2}$ in. by 7	ft. 7 in. by 7 ft.
Waste heat, chimney.....	two, 27 by 11 in.	5 ft. 6 in. top,	42 in. diam., 60	36 in. diam., 100	2 ft. 3 in. by 1 ft.	5 ft. diam. top,
boiler, kind, horsepower.....	25 ft. high	125 ft. high	ft. high	ft. high	9 in., 37 ft. high	145 ft. high
recuperator, surface, square feet.....		vertical water				
regenerator, volume, cubic feet.....		tube, 588 hp.				
Ore, tons 24 hr.....	9	33	2,915	3,814		2,375
Labor, men in 24 hr.....	6		10	20	20	13-14
hours per ton ore.....		1.4	1.03			17@8 hr.
hours per ton spelter.....		2.2	2.40			9
Spelter, pounds 24 hr.....	3,800	20,000	7,700	21,500	17,700	7,000

Zinc Co.; the fuel consumption is not low. The Neureuther type is in the ascending, as it shows the lowest fuel consumption. Of the Rhenish furnaces a modified Overpelt is in use at a single plant; this is in direct contrast to European practice where Rhenish furnaces are favorites and are being introduced into the new zinc plants of Great Britain. Belgian furnaces fired with natural gas are common in gas belts, but even there the price of natural gas has increased to such an extent, say to 7 cts. per thousand cubic feet, that it has become an open question whether a coal plant would not work more cheaply as regards cost of fuel. However, a natural gas plant can be built more quickly and cheaply than a coal plant; and can be transferred more readily from one gas region to another as evidenced by the removal of several zinc smelteries from Kansas to Oklahoma.

108. Results.—A consideration of results obtained in distillation has to deal mainly with the utilization of fuels and refractories and the recovery of metal.

A thermal balance gives a clear idea in what manner the heat producing elements have been utilized. It is difficult to cast such a balance, as it necessitates a great number of observations to be taken simultaneously, numerous complete analyses, and not a few assumptions. The thermal balance of Eulenstein¹ for a Rhenish furnace with Siemens regenerators gives the data shown in Table 35.

TABLE 35.—THERMAL BALANCE OF RHENISH DISTILLATION FURNACE WITH SIEMENS REGENERATORS

Debit	Per cent	Credit	Per cent
Producer gas.....	90.94	Heat in waste gas.....	50.85
Sensible heat in charge.....	0.18	Heat in residue.....	2.67
Burning of C.....	8.74	Heat in spelter.....	0.45
Sensible heat in new retorts....	0.14	Heat in gas from condensers	2.76
.....		Endothermic reactions....	10.96
.....		Sensible heat in discarded	
.....		retorts.....	0.19
		Loss by radiation and con-	
		duction by difference.....	32.12
	100.00		100.00

The thermal balance shows that the greatest loss in heat is caused by the waste gases, and that the loss by radiation and conduction is

¹ *Metallurgie*, 1912, IX, 328, 353, 396.

very large; it points to remedies by which these high values can be diminished. General considerations regarding a thermal balance for zinc distilling furnaces have been published by Chabanier¹ and Sanson.²

The refractories to be considered are those used in lining the fire and combustion chambers and in the manufacture of retorts.

Formerly a furnace had to be relined once a year; at present with better firebrick and more careful firing methods, the life of the lining is 2 years with direct-fired, and 3 years with gas-fired furnaces. The life of a retort made of a given mixture depends upon the character of the ore treated and upon the temperature necessary to obtain complete reduction. Docile oxide ores are easy on retorts; roasted blende being less easy of reduction is likely to attack the retort; this is especially the case if it runs high in Fe, and if the S has been incompletely removed, because ferruginous slag and matte both eat into the clay mixture. A retort made by hand used to last 20 days; made by auger machine the life is a little longer reaching perhaps 30 days; a retort from a hydraulic press lasts as long as 40 days, which corresponds to about $2\frac{1}{2}$ per cent breakage per day. However, retorts in the hotter parts of a furnace last a shorter time than those in the cooler. Muffles last longer than retorts, say 40 to 50 days, as they are not exposed to such high temperatures owing to the docile charges distilled.

The yield of zinc³ in a modern plant is about 87 per cent, and may reach 90 per cent; with ferruginous blende 80 per cent is considered a good extraction but often falls to 75 per cent, the percentage being based on the zinc contained in the charge. Sometimes the loss is referred to the metal in the ore; an ore assaying 50 per cent Zn is said to yield 45 per cent and to give a loss of 5 per cent; with the usual manner of figuring, the loss would be 10 per cent. The loss in zinc is incurred in several ways. The residue in the retorts retains under favorable conditions not less than $2\frac{1}{2}$ to 3 per cent Zn, and the weight of the residue is roughly 50 per cent of the weight of the charge; of course, the weight varies greatly with the character of the ore and the amount and character of the reducing fuel. Zinc is present as ZnS which existed in the ore or was formed in the retort; as Zn_xSiO_y which was not reduced or had been formed; as original ore which was inclosed in slag- or matte-like sintered or

¹ *Rev. Mét.*, 1913, X, 423.

² *Ibid.*, 426.

³ Ingalls, *Eng. Min. J.*, 1917, CIV, 949.

fused matter and thus escaped reduction. The retorts absorb Zn and slag ZnO; they allow zinc vapor to pass through the pores and cracks into the combustion chamber. Broken retorts lose their charges. Zinc vapor is not completely collected and passes off through the condenser and prolong. Table 36 gives some figures of a series of tests carried out in the Belgian direct-fired furnace by J. P. Wetherill in 1889 with different kinds of roasted blende and a given reducing fuel to determine the distribution losses of zinc.

TABLE 36.—DISTRIBUTION OF ZINC IN DISTILLING IN BELGIAN DIRECT-FIRED FURNACE

Charge												
Roasted blende					Reducing fuel mixture							
Lb.	Per cent				Used, per cent	$\frac{1}{2}$ coke jigged from ashes of fireplace, $\frac{1}{4}$ bituminous coal-slack with H ₂ O 0.97, Vol. H-C 18.84, fixed C 55.25, Fe 5.15, S 4.04, ash 24.94.						
	Zn	Fe	S									
5,100	50.75	1.65	0.76	39.5								
4,900	51.48	1.10	0.53	40.0								
4,600	49.71	1.17	0.46	39.2								
4,600	51.89	1.51	0.66	39.2								
Products												
Residue					Broken retorts		Zinc account					
Lb.	Per cent				Lb.	Zn, per cent	Per cent					
	Zn as Zn and ZnO	Zn as ZnS	S	Fe			Spel-ter	In residue		In broken retorts	Total	
								as Zn and ZnO	as ZnS		Account- ed for	Lost
2,880	7.96	4.18	2.77	5.29	501	10.96	84.2	8.8	4.6	1.8	99.4	0.6
2,980	8.35	3.39	2.42	4.12	501	10.96	80.8	9.4	4.5	2.1	96.8	3.2
2,250	5.98	2.22	2.37	5.08	334	10.96	86.1	5.9	2.2	1.6	95.8	4.2
2,210	6.05	2.78	2.38	4.95	334	10.90	82.2	5.4	2.8	1.5	91.9	8.1
						Average	83.3	7.4	3.5	1.7	95.9	4.1

Losses of silver and gold in treating ores containing precious metals¹ are very small. With Butte & Superior ore assaying Zn

¹ Ingalls, *Eng. Min. J.*, 1919, CVII, 87.

50.5 to 53.2, Fe 2.4 to 4.7, Mn 0.22 to 1.00, Pb 2.4 to 3.6, Cu 0.33 to 0.50, Insol. 11.6 to 14.1 per cent, and Ag 14.0 to 18.5 and Au 0.03 oz. per ton, $2\frac{1}{2}$ tons concentrates with 40 oz. Ag per ton were required to obtain 1 ton spelter; of this 35 per cent with 0.164 oz. Ag per ton and 1 per cent Pb was obtained in the first draw, 50 per cent with 0.538 oz. and 1.5 per cent in the second, and 15 per cent with 1.178 oz. and 2.25 per cent in the third.

The item of labor has been given in Table 34.

The cost of smelting in the Central Western States before the war showed a range of from \$9 to \$12 a ton of ore depending upon the size of plant. At present it is twice as much, and reaches even \$30 a ton. Estimates of cost of smelting at the Bertha works, Virginia, by Moxham¹ and in the Joplin district by Hedberg² give details of conditions prevailing 30 years ago.

109. Products.—General.—The products of distillation are retort gases, crude zinc, blue powder, residue from retort, residue from condenser, old retorts, and old condensers.

110. Retort Gases.—The gas issuing from the retorts contain mainly CO that is 97 to 98 per cent; if CO₂ were present to any extent, zinc vapor would be oxidized (see §5). When a charged retort is being heated, the gas issuing at first from the throat is rich in CO₂, 13 to 25 per cent vol., on account of the presence of air and the prevailing low temperature. As the temperature is raised, C burns more and more to CO instead of CO₂, and above 1,000°C. CO is formed exclusively. Table 37 gives the analyses of Fischer³ from retorts of Letmathe, Westphalia.

TABLE 37.—RETORT GASES FROM LETMATHE, WESTPHALIA

Constituent	1	2	3	4	5	6	
CO ₂	15.58	0.48	9.06	0.11	1.10	0.82	Sample 1: before distillation
CO.....	38.52	n.d.	92.16	97.12	n.d.	98.04	Sample 2: beginning of distillation
H.....	41.70	5.32	1.83	n.d.	n.d.	0.72	Sample 6: just before end of distillation
N.....	tr.	n.d.	1.01	0.41	n.d.	tr.	
CH ₄	4.17						

¹ *Eng. Min. J.*, 1893, LVI, 544.

² *Mines & Minerals*, 1898, XIX, 103.

³ *Dingl. Polytech. J.*, 1880, CCXXXVII, 390; *Berg. Hüttenm. Z.*, 1880, XXXIX, 371.

The results of an extended investigation by Mühlhaeuser¹ into the compositions of gases from a Hegeler furnace at La Salle, Ill., treating charges with 58.2 lb. roasted blende (71.0 per cent Zn)

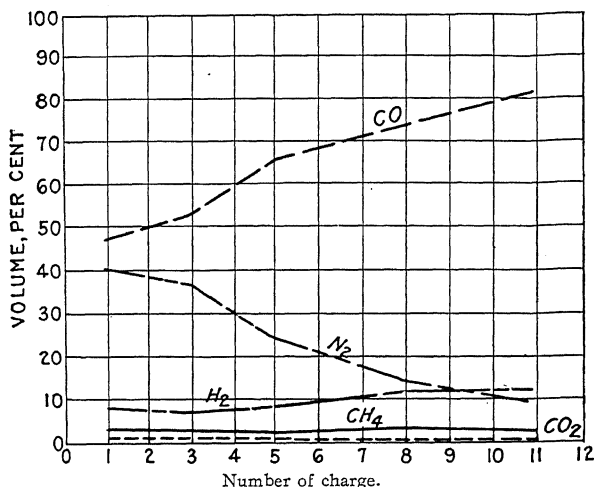


FIG. 178.—Analyses of retort gases five hours after charging.

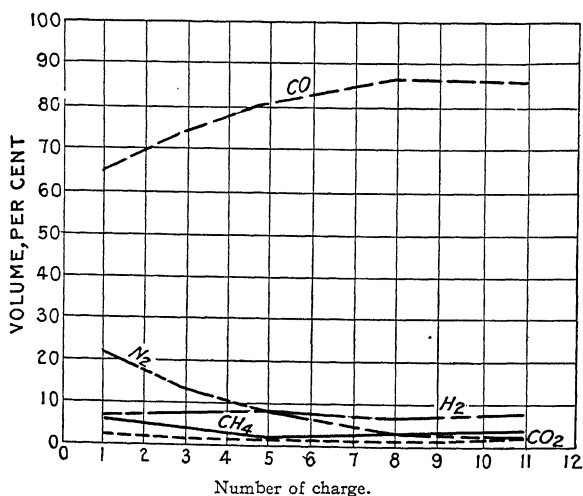


FIG. 179.—Analyses of retort gases twenty-two hours after charging.

and 25.6 lb. anthracite are assembled in Figs. 178 and 179. The abscissæ represent the number of charge lasting from Charge 1 to 11; the ordinates, volume percentages. Figure 178 gives the

¹ *Metall u. Erz.*, 1918, xv, 431.

results obtained 5 hr. after charging, *i.e.*, when the gas burned with a blue flame and the reduction of ZnO had begun; Fig. 179 the results 2 hr. before the distillation was ended. The curves show that in the reduction of ZnO there is formed mainly CO; that there is a diminution of CH₄, N and of CO₂ with the progress of the distillation owing to the coking of anthracite; that furnace gases (CO₂, N, H) enter the retort and act upon C and Zn vapor; that the entrance of gases, large at first, diminishes with the age of the retort up to the eighth day and then remains constant. Other gas analyses have been published by Firket.¹

III. Crude (Rough) Zinc.—Zinc obtained from a retort is likely to be contaminated with metals such as Pb, Fe, Cd, Cu, As, Sb, with S and Si, and to enclose drosses, oxides, carbonaceous matter, all of which interfere with its industrial uses. Steger² and Prost³ give analyses of crude zinc of which a few are reproduced in Table 38.

TABLE 38.—CHEMICAL ANALYSES OF CRUDE ZINC

Element	Steger				Prost		
	Silesia		Saxony		Belgium		
Zn.....	98.452	98.296	97.3340	98.054	98.5085	96.778	96.267
Pb.....	1.493	1.672	2.6140	1.03	0.70	2.56	3.43
Fe.....	0.033	0.023	0.0300	0.04	0.68	0.33	0.17
Cd.....	0.018	0.004	0.0206		0.03	0.24	0.10
Sn.....				0.07			
As.....	0.002		0.0014	tr.	0.03	0.005	0.003
Sb.....					0.01	0.007	
Ag.....	0.002				0.0005		tr.
Cu.....					0.009	0.02	0.03
C.....		0.005			0.002		
S.....					0.01		tr.
Si.....					0.02	0.06	

Spelter produced in the United States is mostly of a higher grade (see Table 6a) than that of the European examples shown.

The usual method of refining crude for commercial spelter⁴ is that of liquation in a reverberatory furnace. As the separation of lead from crude zinc by this operation, *e.g.*, from prime Western

¹ *Ann. Min. Belg.*, 1901, VI, 49.

² "Verdichtung der Metaldämpfe in Zinkhütten," Enke, Stuttgart, 1896, pp. 76 and follow.

³ *Op. cit.*, p. 127.

⁴ Kerl, *Mineral Ind.*, 1896, V, 611.

with $1\frac{1}{2}$ per cent Pb, does not go far enough, the metal may have to be refined by redistillation. Zinc from galvanizing drosses, *e.g.*, is recovered in this way (see §113). Electrolytic refining of crude zinc has been tried; it is not economically successful in comparison with distillation. A plant of the Electrolytic Zinc Co. working according to the patents of C. H. Aldrich and J. K. Bryan¹ and H. M. Stuart² was in operation during the World War, when the difference in price between ordinary and electrolytic spelter was sufficient to pay for the cost of treatment and leave an appreciable profit.

112. Refining Crude Zinc in the Reverberatory Furnace.³—In melting crude zinc at a low temperature, there rise to the surface non-alloyed impurities and oxides which have a lower specific gravity than zinc; they form a dross which is removed by skimming and goes back to the distillation furnace; there sink to the bottom most of the Pb and Zn-Fe alloy (§10). Zinc at its melting point holds in solution (§9) about 1 per cent Pb; spelter from lead-bearing crude zinc retains about this amount of lead and 0.030 to 0.040 per cent Fe. The liquid lead holding 2.3 per cent Zn in solution at 500°C. (Table 7) is removed at intervals from the bottom of the furnace as is the mushy Zn-Fe alloy floating on top of it. An assay of such lead gave Steger⁴ Zn 4.2400, Cd trace, Fe 0.0008, Pb 95.7592 per cent, showing that the temperature of the metal bath must have been in the neighborhood of 700°C. (Table 7). The lead is usually sold to lead refiners who desilverize lead bullion by the Parkes process;⁵ it can be refined in the plant in a reverberatory furnace or a kettle but usually there is not enough of it to make the procedure profitable.

Zn-Fe alloy contains 5 to 6 per cent Fe; it is sold to refiners of galvanizing scrap who distil it as shown below.

The reverberatory furnace in which crude zinc is liquated has a low arch spanning an oblong hearth which slopes from fire bridge to flue where there is a sump and a ladling door. The capacity shows a range from 20 to 150 tons. The crude spelter produced in the United States is usually sufficiently pure to make liquation unnecessary. Liquating furnaces are confined to rolling mills which have to remelt the spelter for casting into plates of different sizes.

¹ U. S. Patent No. 1,299,414, Apr. 8, 1919.

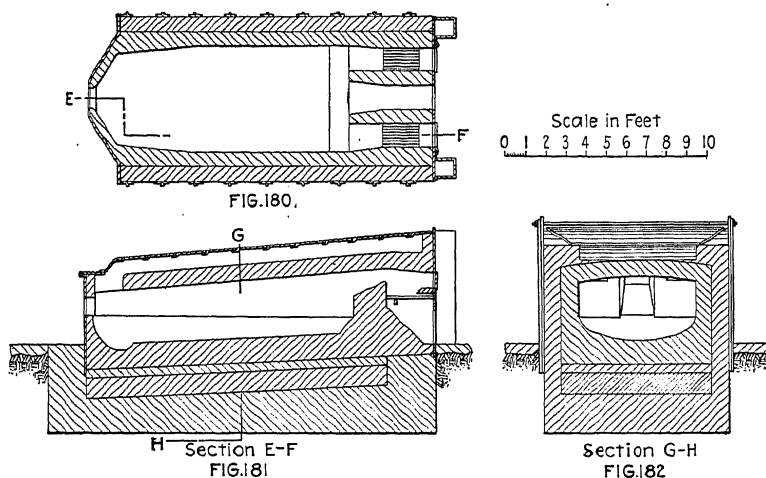
² British Patent No. 108,311, Jan. 10, 1918.

³ Wemple, *Tr. A. I. M. E.*, 1918, LIX, 183.

⁴ *Op. cit.*, p. 78.

⁵ Hofman, "Lead," 1918, p. 494.

The furnace used in Silesia,¹ shown in Figs. 180 to 182, has the charging door at one end with fireplace on either side; the fire gases pass out over the hearth, return in a flue above the roof and enter the chimney. The hearth is 15 ft. 5 in. long, 6 ft. 6 in. wide, slopes from fire bridge to ladling door about 3 deg., the lowest point is 1 ft. 8 in. below the door. The brick hearth is lined with a mixture of raw and burnt clay, holds from 20 to 30 tons zinc, and refines 9 to 10 tons in 24 hr. with a consumption of about 10 per cent coal.



FIGS. 180, 181 and 182.—Liquation furnace for crude spelter.

The furnace of the Hohenlohe works, Silesia,² is similar; it is 19 ft. 8 in. long, 10 ft. 6 in. wide, and holds 30 tons zinc. In our day the hearth of the furnace would be built into an iron pan, it would be of brick and not of a mixture of raw and burnt clay.

Starting a new furnace requires the usual warming. When warm, the 20 to 30 tons zinc necessary to fill the hearth are charged and melted in 2 to 3 days, as the temperature has to be kept low; if melted more quickly the bath has to stand 18 to 24 hr. to allow the lead and iron to settle. In firing, the flame is kept smoky to avoid oxidation as much as possible. When the furnace is filled, floating dross is skimmed onto the sloping plate of the charging door, freed from adhering particles of zinc by working in perhaps 0.25 per cent of ammonium chloride, and withdrawn. The dross amounts

¹ Thum, *Berg. Hüttenm. Z.*, 1873, XXXII, 290.

² Schmieder, *Oest. Jahrb.*, 1889, XXXVII, 389.

to about 1.25 per cent of the weight of the zinc. The fine zinc is now ladled from the sump at the rate of 9 to 10 tons in 24 hr., and a corresponding amount of crude zinc charged at the other end of the furnace. Thus the level of the metal bath is kept approximately constant. The surface has to be drossed once in 12 hr. When sufficient lead has accumulated on the bottom, or when the lead and iron accumulations have risen to 12 in. beneath the zinc, the lead is removed, *i.e.*, about once a week, by an Archimedian screw in a cast-iron pipe¹ or by thrusting into the bath an iron tube closed at the lower end with a clay plug, knocking out the plug, and ladling the rising lead.² A more simple method is to tap the lead in the usual way. The mushy Zn-Fe alloy is removed at times with a perforated shovel, when the furnace has to be emptied for the sake of repairs or other reasons. The zinc in the products from refining crude spelter with 1 per cent Pb is distributed about as follows: refined spelter 91.5 per cent, dross and skimmings 5.5 per cent, lead 1.5 per cent, loss 1.5 per cent. The refined zinc is cast into iron molds placed in a semicircle or on a traveling carriage or on a horizontal casting wheel. The casting temperature ought to be low, as slowly cooled metal is fibrous; it is coarsely crystalline when cooled quickly.³

Samples of spelter⁴ for analysis are obtained by drilling or granulating. Plates cast from each draw are drilled, aliquot parts are mixed and a final sample of not less than 20 g. taken for an assay. Parts of the contents from one or two ladles of each draw are granulated. Granulation avoids contamination with steel from the drill.

113. Refining Crude Zinc by Distillation.⁵—In distilling crude zinc there is obtained the refined spelter with 99.9x per cent Zn. The cost of operating is estimated by Ingalls to be 0.5 to 1.0 ct. per pound; the loss in zinc is about 5 per cent. If the premium for the higher grade metal makes up for the cost, loss, and non-use of retorts for ore, the operation will be profitable.

Usually the ore furnace serves for distillation, using three or four rows of retorts. The inclination of retorts, which have to point upward if they are to hold a bath of metal, is changed by removing

¹ Föhr, *Berg. Hüttenm. Z.*, 1883, XLII, 14.

² Schmieder, *Oest. Jahrb.*, 1889, XXXVII, 402; *Berg. Hüttenm. Z.*, 1890, XLIX, 130.

³ Job-White, *Proc. Am. Soc. Test. Mat.*, 1915, XV², 112; *Iron Age*, 1915, XCVI, 199.

⁴ Johnson, *Met. Chem. Eng.*, 1918, XVIII, 135.

⁵ Ingalls, *Eng. Min. J.*, 1915, C, 488.

Wemple, *Tr. A. I. M. E.*, 1918, LIX, 176.

the bottom row of retorts and lowering the butts of the upper row onto the shelves of the next lower rows. The temperature maintained is of course lower than in ore distillation. The condensers used differ from those that are used with ore. At some works the ordinary condenser is partly closed at the larger end by a semi-circular dam; at others the condenser has the form of a truncated cone 7 and 10 in. in diameter, the smaller end provided with a dam is luted into the throat of the retort, while the larger is closed with a fire plate having an opening at top and at bottom, the openings being stuffed as is the nose of the ordinary condenser. The crude spelter is either broken into pieces or cast into sticks 20 in. long, 1.5 by 1 in. in section, weighing about 10 lb.; four or five sticks make a charge. The condensers are drawn every 4 or 6 hr.; in drawing, the top hole is spied to relieve the pressure, then the bottom hole is opened to remove the metal and blue powder. The distilled metal is melted in a reverberatory (equalizing) furnace and then cast. The residue in the retort is removed periodically with a large scraper after taking off the condenser. Rare metals, such as Ga, Ind, and Ge have been found in the residue.¹

De Saulles uses a furnace which has retorts on one side only; the retorts are inclined about 7 in. and extend through the back wall for 4 or 5 in. At the butt end on the top they have an opening for receiving molten zinc, and another at the bottom for tapping the lead. The crude zinc, refined in a reverberatory furnace, is drawn off into a ladle by cutting into the clay dam which closes the tapping slot; the ladle suspended from an overhead trolley is brought to the back of the distilling furnace and its content emptied into the retort. Retorts are charged once in 24 hr.; condensers are drawn every 4 hr.; the distilled metal collected in a traveling ladle is discharged into an equalizing reverberatory furnace; the leady metal is tapped once in 24 hr., 2 hr. before recharging; every 10 days the retorts are tapped dry. Once in 2 or 3 weeks the lead in the remelting furnace is removed by tapping.

The re-distilling furnaces receive crude spelter from the second or third draws with 1.5 to 3 per cent Pb, 0.03 to 1.0 per cent Fe, 0.03 to 0.07 per cent Cd, or refined spelter with about 1.00 per cent Pb and 0.03 to 0.05 per cent Fe. The redistilled spelter averages 0.10 per cent Pb, 0.01 Fe, 0.04 Cd, 99.85 Zn. The zinc recovery is redistilled spelter 80 per cent, by-products 15 per cent, loss 5 per cent. The loss is caused mainly through the retorts which last

¹ Ingalls, *Min. Ind.*, 1916, xxv, 778.

60 days when made in a hydraulic press, and 20 to 30 days when in an auger machine.

Distillation in electrically heated furnaces is in operation at Trollhättan, Norway.¹

114. Refining Galvanizer Dross.²—The dross which collects on the bottom of a galvanizing kettle contains about 96 per cent Zn and 4 per cent Fe. It is pasty at the melting point of zinc, and is removed by means of a perforated spade-like ladle and cast into molds. Two methods for the recovery of the zinc are in use. Fusion with fluxes (Richards) and distillation.

The Richards method³ consists in melting the dross in a kettle with the addition of potassium cyanide and sulphur. As potassium cyanide is too expensive, it has been replaced by raw potatoes and scrap leather, the potatoes to furnish steam for stirring, and leather the cyanide. The dross is melted in a kettle, and the flux mixture thrust into the bath in small quantities by means of a bell-shaped iron receiver with handle. The bath is kept in constant ebullition for from 15 to 30 min.; the dross that rises to the surface is skimmed, the refined metal drawn, and the matte which had settled on the bottom removed. The zinc is contaminated with oxide. In order to reduce the oxide, there is added to a kettleful of zinc an equivalent of 0.001 per cent Al in the form of an alloy of Zn 95, Al 5 per cent; the quantity of alloy required is 0.5 lb. of zinc. The zinc made contains Zn 98.35, Pb 1.50, Fe 0.15 per cent.

The Distillation Method.—In distilling galvanizing dross, the character of the raw material requires a larger retort than the one used for ore and crude zinc. The furnace designed by Engle⁴ is shown in vertical section in Fig. 183. Eight pear-shaped graphite retorts are placed around a central stack; each retort has its fireplace, the flame surrounding the upper part is drawn downward to the bottom before it enters the stack. A retort, No. 8 of the Dixon Crucible Co., is 35.5 in. long, has a diameter $8\frac{7}{8}$ in. at the neck, 20 in. at the belly, and 14 in. at the bottom; its thickness is $2\frac{1}{2}$ in. at the bottom, $1\frac{3}{4}$ in. at the belly, and $1\frac{1}{8}$ in. at the neck; it is placed to form an angle of 25 deg.; and holds a molten charge of about 700 lb. The cylindrical clay or graphite condenser, is 29 in. long and $8\frac{3}{4}$ inner diameter, it has walls $1\frac{1}{2}$ and 2 in. thick, and the usual vent

¹ *Chem. Abstracts*, 1916, X, 1813.

² Sperry, *Brass World and Platers Guide*, 1906, II, 409.

³ *Jour. Frank. Inst.*, 1901, CII, 445.

⁴ *Eng. Min. J.*, 1916, CII, 213.

and tapping holes. A charge of 700 lb. dross is distilled in 18 hr. with a consumption of 1,500 lb. of coal per net ton of dross; two men on a shift attend the furnace, the work being so divided that one man looks after four retorts. The life of a retort is from 40 to 65 charges. The yield in metal, 99.9% per cent pure, ranges from 75 to 88 per cent, depending somewhat upon the grade of dross treated, whether it has been previously sweated or not. In the presence of cadmium, the first draw weighing about 50 lb., will contain the major portion of the cadmium, the second draw rarely assays more than 0.0045 per cent Cd.

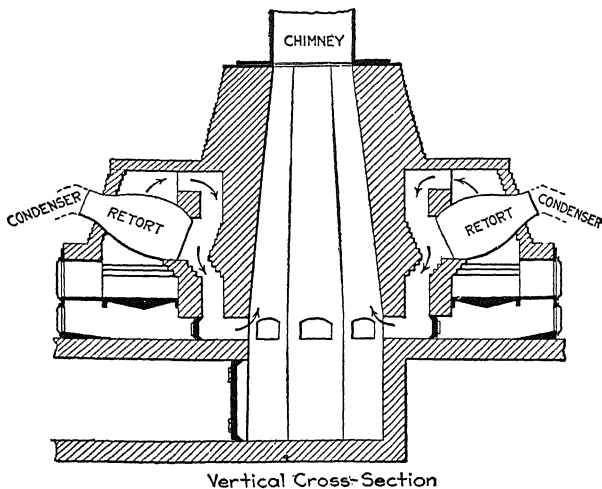


FIG. 183.—Engle furnace for distilling galvanizer dross.

In some instances galvanizer dross is distilled in the four lower rows of retorts of an ore furnace, but condensers larger than normal are used to take care of the larger amounts of zinc produced.

115. Blue Powder (Poussière). *Residue of Condensers, Etc.*—This bluish powder is made up of finely divided metallic zinc, the particles being more or less coated with zinc oxide; it contains from 88 to 93 per cent Zn, 6 to 10 per cent ZnO. In addition there are present volatile metals such as Pb, Cd, As, and Sb, and some Fe and insoluble residue. In redistilling spelter, De Saulles¹ has purposely produced blue powder on account of its extended use as a

¹ *Chem. Abstr.*, 1917, XI, 935; Anon., *Eng. Min. J.* 1917, CIII, 788.

precipitant in cyaniding gold and silver ores.¹ Analyses of Belgian, Silesian, and Austrian blue powder are given in Table 39.

TABLE 39.—ANALYSES OF BLUE POWDER

	Belgium			Silesia			Austria		
Zn, total.....	94.04	90.11*	95.50						
Zn, metal.....	88.74		85.34	84.463	88.50	86.60	90.70	29.59	40.00
ZnO.....	6.60			4.888	7.40	7.70	3.90	57.74	49.80
ZnCO ₃									3.30
Pb.....	2.50	0.82	1.50	4.276	2.02	3.55	2.93	tr.	2.50
Fe.....	0.30							2.05	
Fe ₂ O ₃				0.903	0.06	0.09	0.10		
Cd.....	1.30	0.005		2.654					4.00
CdO.....					1.84	1.62	1.83		
As.....		none						0.32	
Sb.....		none						0.37	
CaO.....				2.464					
MgO.....				0.239					
S.....								0.03	
Ins. & C.....	0.50	3.33	2.5	0.120		0.35			0.40
Reference.....	1	1	1	2	2	2	2	3	3

1. Firket, *Ann. Min. Belg.*, 1901, VI, 51.

2. Steger, V, "Verdichtung der Metaldämpfe in Zinkhütten," Enke, Stuttgart, 1896, p. 80.

3. Lainer, *Oest. Zt. Berg. Hüttenw.*, 1894, XLII, 25.

* Contains a little ZnO.

The presence of non-volatile substances is due to their being carried over by zinc vapor; Jensch² gives a chemical explanation as regards Fe.

In Europe blue powder was formerly heated under pressure in boot-like closed vessels³ in order to remove by liquation the metal, but this has been abandoned. Electrolytic reduction with ZnCl₂ as fused electrolyte, Acheson graphite as anode, and an iron kettle as cathode has been advocated by Becker.⁴

At present the blue powder is usually added to charges that are treated in cooler parts of the distilling furnace. The impurities it contains are made harmless by being distributed through a large

¹ Herz, *Tr. A. I. M. E.*, 1915, LII, 138.

² *Eng. Min. J.*, 1890, I, 647.

³ Montefiore furnace, Landsberg, *Rev. univ. Min.*, 1858, III, 1.

Thum, *Berg. Hüttenm. Z.*, 1859, XVIII, 409.

⁴ *Met. Chem. Eng.*, 1912, X, 300.

quantity of ore. If the powder is rich enough in Cd to make it worth while, it is reserved for the recovery of this metal (see §156). The following analysis by Mühlhaeuser¹ shows the concentration of Cd in the first blue powder form in working roasted blende; Zn 43.72, Cd 11.74, Fe 1.52, C 28.84.

Blue powder is used² to a considerable extent in chemical industry; the Cowles galvanizing process is based on it; in precipitating silver and gold from cyanide solutions it has largely replaced filiform zinc; in the electrolysis of zinc sulphate it finds application in the purification of the electrolyte (§128). In shipping, blue powder has to be packed in air- and water-tight vessels as it hardens and there is danger of self-ignition.³

Residues from Condensers, Drippings, Skimmings, Sweepings, Etc.—The condensers are coated on the inside with blue powder and oxide, and retain metallic zinc; they are scraped and the scrapings added to the furnace charges. The same is the case with the scrapings from retorts, floor sweepings, gray and white oxides formed by the oxidation of zinc fume issuing from the condensers and saved in prolongs and fume collectors; all zinc-bearing intermediary products, drippings, receive the same treatment.

116. Residues from Retorts.⁴—These residues, also called cinders, consist of coked reducing fuel and non-volatile components of the ore. Their compositions vary greatly with the characters of the ore treated; they contain perhaps 2 to 7 per cent Zn, 1 to 10 per cent Pb, 3 to 20 per cent Fe, 2 to 6 per cent CaO and MgO, 50 ± per cent C and insol. residue, often Ag and Au. The presence of Ga and Ge is noted by Fogg and James.⁵ Analyses of raw and concentrated cinder from 11 Belgian plants have been published by Firket.⁶

Their treatment is governed largely by the presence or absence of Pb containing Ag and perhaps Au. If they have little value they go to the dump, as wet concentration with the idea of saving fuel does not pay.⁷ With lead-bearing cinder dry screening through a 5- or 6-mesh sieve may be profitable, as it removes the coke and

¹ *Metall u. Erz.*, 1919, XVI, 70.

² Speier, *Min. Sci.*, 1911, LXIII, 38.

³ Speier, *Oest. Zt. Berg. Hüttenw.*, 1906, LIV, 39.

⁴ Johnson, *West. Chem. & Met.*, 1905, I, 179; *Eng. Min. J.*, 1906, LXXXI, 318; *Met. Chem. Eng.*, 1918, XVIII, 135.

Mühlhaeuser, *Metall u. Erz.*, 1918, XV, 260.

⁵ *Jour. Am. Chem. Soc.*, 1919, XLI, 497.

⁶ *Ann. Belg.*, 1901, VI, 55.

⁷ Steger, *Zt. B. H. U. S. W. i. Pr.*, 1896, XLIV, 447.

thereby enriches the undersize in Pb and Fe.¹ Wet concentration is a common operation for obtaining an enriched lead product which goes to lead blast furnaces. Here it is an unwelcome component of the charge, as the ZnS present causes much trouble. It is rarely smelted alone.²

Lead-free residue is screened at Cherryvale, Kan., to pass a sieve with $\frac{5}{8}$ -in. openings and remain on a 20-mesh screen. The oversize from the $\frac{5}{8}$ -in. sieve goes to the spelter furnace being high in Zn, the material between $\frac{5}{8}$ -in. size and 20-mesh screen goes to steam boilers having under-grate blast.³

Burnt residue forms a more satisfactory addition to the lead blast-furnace charge. At the Bartlesville Plant No. 2 of the Bartlesville Zinc Co., Bartlesville, Okla.,⁴ the residue is burned in heaps, the temperature being kept high by blast to sinter the material when it has been freed from C. Residues are mixed so as to furnish a product with over 5 and under 10 per cent lead. Thus Butte residue containing Zn 10.2, Fe 7.2, Mn 0.7, Pb 4.7, insol. 30.0, Cu 0.6, C 35.0, Ag 37 oz., is mixed with residue from Coeur d'Alene, Zn 7.5, Fe 11.0, Mn 0.4, Pb 9.0, insol. 27.5, Cu 0.2, C 30.0, Ag 6 oz., to furnish a clinker with Zn 12.9, Fe 12.9, Mn 1.1, Pb 9.8, SiO₂ 38.0, Cu 0.8, C 1.2, Ag 27 oz. The balance sheet from several years shows in percentage: shrinkage in weight 32, Au -0.8, Ag -3.2, Cu +1.4, Pb -8.9, Zn -18.1, Fe -2.8, Mn -7.2. The losses in Ag, Pb, and Zn are due to volatilization; those in the other metals to dusting. The heaps, 47 to 50 ft. square at the bottom, and 17 in number, are arranged in a long row which are skirted on one side by the air main, 30 in. in diameter, and at the other by a track for a locomotive crane and railroad cars, Fig. 184. From the air main, 12-in. pipes branch off to the heaps. A pipe, provided with a slide gate, ends in a Y-shaped brick flue with 8-in. passages built of brick or tile bats laid in cement and covered with earth for protection; the limbs conduct the air into two headers, 4 by 4 in. in size. A brick header (see section BB) is built four courses high and 4 in. apart in the central third, and three courses high in the other two; the roof is of brick or tile laid closely. From the header 13 channels, section AA, are laid out over leveled floor; the bottom course is laid dry, while the

¹ Johnson, *Met. Chem. Eng.*, 1918, XVIII, 136.

² Johnson, *Eng. Min. J.*, 1906, LXXXI, 318; *Met. Chem. Eng.*, 1918, XVIII, 139.

³ Ingalls, *Min. Ind.*, 1914, XXIII, 796.

⁴ Leslie, *Min. Sci. Press*, 1914, CIX, 48.

Stock, *Chem. Met. Eng.*, 1919, XX, 525.

top course and roof are made airtight. The headers and channels are covered with a thin ridge of earth which is patted down. The former method of operating, which is still in use to some extent, was to drop from an elevated track a layer of hot residue and admit some air; when burning, more residue was charged until the heap had reached a height of about 6 ft. and held 400 tons; it burnt about

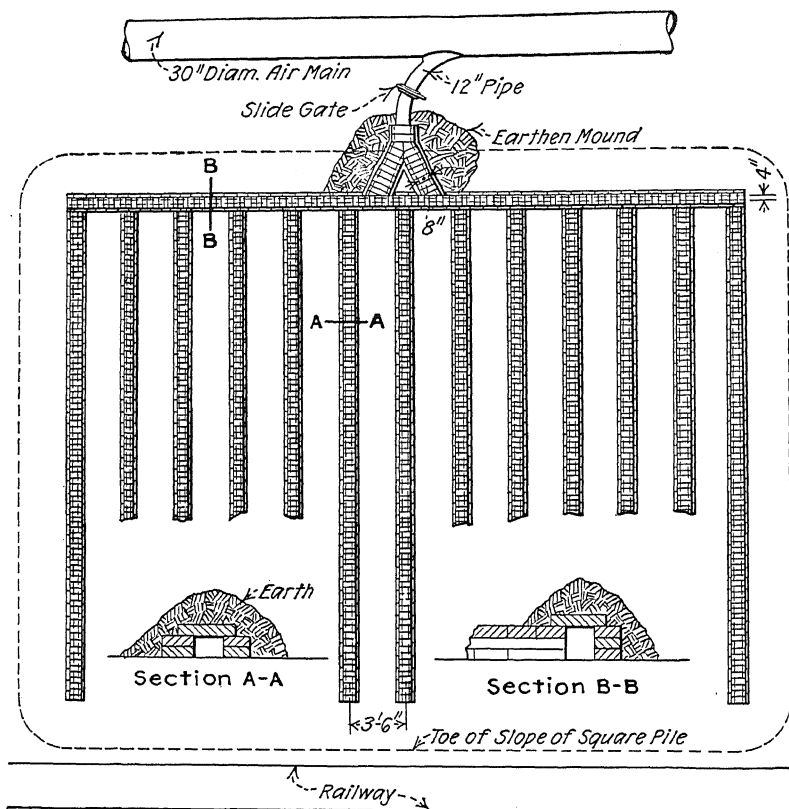


FIG. 184.—Plan for clinkering heaps, Bartlesville.

40 days. At present about 100 tons residue are unloaded from cars by a locomotive crane and clam-shell bucket in a ridge covering the header of a heap. Two more carloads are discharged at the opposite ends leaving open a trough across the channels. Cord wood is piled between the channels, some hot coals are placed on the wood, and the whole covered with residue from adjoining heaps. Air from a No. 10 Sturtevant blower is

admitted; when the wood burns freely, two more cars of residue are unloaded to fill the trough. Full air is turned on, and the heap leveled and trimmed to a height of about 5 ft. Within a week the heap is fully kindled, the central part which has shrunk is leveled and kept level with fresh residue amounting in all to 4 or 6 extra carloads. A heap holding 500 to 600 tons residue is burned through in 35 days being inspected every day, blow holes are closed, etc. A burnt heap is sprinkled for 3 days, holes are driven with bars and blasted with dynamite; the cakes are loaded into cars and shipped. The row of 17 heaps furnishes monthly 40 to 45 cars of clinker or 2,100 tons. The daily cost is \$107 or \$1.53 per ton of clinker.

In some plants, *e.g.*, Hillsboro, Depue, Ill., and Donora, Pa., the Wetherill grate (§140) is used to oxidize the carbon and to recover the zinc and lead fumes in a baghouse as the pigment, or as an oxide to go back to the spelter furnaces. The loss in lead is likely to be over 20 per cent, and that of silver under 10 per cent. It has been suggested that the presence or addition of copper might diminish the loss in silver. The addition to the charge of 25 per cent coarse sand or tailing is said to greatly reduce the loss. The residue on the grate is sometimes screened to obtain a coarse product ready for the lead blast furnace, and fine material to be incorporated in another charge. The cost is said to be about \$2 a ton.

At the works of the Edgar Zinc Co., residues are mixed with 20 per cent coal and used as a boiler fuel.¹

Electromagnetic experiments have been carried out by Lindt² who treated residue with Zn 3.8, Pb 0.56, Fe 18.9, S 4.73 per cent, and 114 oz. Ag per ton. He obtained 26 per cent magnetic material with Zn 3.8, Pb 0.16, Fe 59.6, S 3.65 per cent, and 338 oz. Ag per ton, and 74 per cent non-magnetic with Zn 3.8, Pb 0.71, Fe 4.6, S 5.12 per cent, and 46 oz. Ag per ton.

117. Old Retorts and Condensers.³—Retorts undergo considerable changes while in use in the furnaces. They become more or less charged with zinc oxide; auger retorts retain about 16 per cent of ZnO, when made in the hydraulic press they retain 6 to 10 per cent ZnO. The ZnO combines with SiO₂ forming willemite (2 ZnO·SiO₂),

¹ Ingalls, *Min. Ind.*, 1913, XXII, 805.

² *Metall u. Erz.*, 1913, X, 347; *Eng. Min. J.*, 1913, XCVI, 119.

³ Stelzner-Schulze, *Berg. Hüttenm. Z.*, 1881, XL, 145, 150.

Steger, *Zt. B. H. S. W. u. Pr.*, 1887, XXXV, 165; *Berg. Hüttenm. Z.*, 1887, XLVI, 274; *Tonind. Z.*, 1904, XXVIII, 154, 174; *Tr. Am. Cer. Soc.*, 1905, VII, 277.

Proske, *Metall u. Erz.*, 1914, XI, 333, 377, 412, 553.

Schmidt, *Min. Sci. Press*, 1915, CX, 176; *Tonind. Z.*, 1915, XXX¹, 233.

and with Al_2O_3 forming zinc spinel ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$). The retort changes in color, becoming bluish. Stelzner-Schulze found that the outer part of the retort was glazed with zinc silicate of the composition: ZnO 56.11, Fe_2O_3 0.81, SiO_2 42.7 per cent; in the blue-colored part they distinguished three substances: zinc silicate (ZnO 5.63, FeO 3.09, SiO_2 2.29 per cent, CaO , MgO and Alk. trace), blue zinc spinel (ZnO 42.60, Al_2O_3 55.61 per cent), and a crystalline aggregate of tridymite and quartz. It is generally held that the bluish part is less refractory than the rest; this is challenged by Steger who holds that it gives additional strength and reduces the absorption of zinc to a minimum. Formerly old retorts used to be freed from adhering slag, then crushed and used as burnt clay in the retort mixture; at present the cleaned retort usually goes into the condenser mixture. At some plants it does not pay to clean them carefully, so they are discarded.

Old condensers are scraped to remove the adhering metal-bearing crusts. The front ends of cleaned condensers are broken off, ground, and washed on a table machine, *e.g.*, the Butchart; the concentrate goes to the ore charge and the tailing to the clay mixture for inferior brick. The butt ends are broken to say $\frac{1}{2}$ -in. size with a hammer and added to the ore charge.

SMELTING IN THE BLAST FURNACE

118. General.—The high cost of treatment and the comparatively low yield of zinc by distillation prompted metallurgists early in the nineteenth century to experiment with the blast furnace, but all attempts have failed and are not likely to be successful. The main work has been done with mixed sulphide ores. A list of the different processes with some details is given by Liebig.¹ The reasons for the adverse results are the difficulties encountered in burning the C of the coke exclusively to CO , in preventing CO from acting as a reducing agent and H_2O -vapor from oxidizing zinc vapor, and lastly in collecting as liquid zinc from the large volume of zinc vapor diluted with inert gas. Zinc vapor, when not oxidized in part, can be collected in a finely divided state. The experiments of Hempel² throw light upon this subject.

119. Lungwitz Process.—In 1896 Lungwitz³ proposed to smelt oxidized zinc ore under the pressure of from 30 to 45 lb. per square

¹ "Zinc und Cadmium," Spamer, Leipsiz, 1913, pp. 505 to 531.

² *Berg. Hüttenm. Z.*, 1893, LII, 355, 365.

³ *Berg. Hüttenm. Z.*, 1896, LV, 329; 347.

inch which was to prevent the volatilization of zinc, permit its collection in a crucible, and its removal by means of a form of Arents syphon tap. Barus had found that zinc boiled at $1,034^{\circ}\text{C}$. under a pressure of 30 lb., and at $1,500^{\circ}\text{C}$. under one of about 741 lb. Early experiments were unsuccessful. The process was tried again at Warren, N. H., in 1906¹ in a furnace which was air-tight at 80 lb. pressure, but failed again. If nothing but zinc vapor were present in the furnace gas² a pressure of 45 lb. might perhaps be sufficient to prevent vaporization of zinc at the prevailing temperature which was about $1,100^{\circ}\text{C}$. and above the reduction temperature of ZnO. In the blast furnace there are present gases and other vapors than those of zinc, each exerting its own partial pressure; the total pressure necessary to keep zinc liquid is from seven to nine times as large as the partial pressure of zinc.

120. Smelting for Zinc Oxide.—If the production of metallic zinc in the blast furnace is improbable, the smelting for zinc oxide is promising. The zinc oxide passing off from the throat of the furnace can be recovered from the gases by a centrifuge, a bag-house, or perhaps a Cottrell precipitator. The oxide would form a rich zinc ore which compressed or compacted, as in the Bartlett process,³ can be treated in the zinc distilling furnace. The experiments of Hempel⁴ along this line endeavor to give valuable fundamental facts.

SMELTING IN THE ELECTRIC FURNACE

121. General.⁵—The low heat efficiency of a closed-vessel furnace, estimated in case of retorts by Richards⁶ at under 7 per cent, prompted metallurgists to replace the usual external heating by internal heating with electric current.⁷ So far electric smelting

¹ Gordon, *Eng. Min. J.*, 1906, LXXXI, 795; LXXXII, 71.

Johnson, *Min. Met. Soc. of Am.*, 1915, *Bull.* 90, p. 247; *Met. Chem. Eng.*, 1916, XIV, 105.

² Editor, *Electrochem. Met. Ind.*, 1905, III, 408.

³ Hofman, "Lead," 1918, p. 132.

⁴ *Loc. cit.*

⁵ Stansfield, E., "The Electric Furnace," McGraw-Hill Book Co., Inc., New York, 1914.

Ingalls, *Tr. Can. Min. Inst.*, 1912, XV, 101; *Met. Chem. Eng.*, 1912, X, 481; *Tr. Electrochem. Soc.*, 1914; XXV, 169.

⁶ "Metallurgical Calculations," McGraw-Hill Book Co. Inc., New York, 1918, Part I, p. 109.

⁷ Ingalls, "Distillation vs. Electric Smelting," *Eng. Min. J.*, 1912, XCIV, 1109.

has been a commercial success only in Sweden and Norway where power is to be had at a low cost.

The earliest experiment is probably that of Cowles Brothers at Cleveland, Ohio, in 1885¹ who used as a furnace a clay cylinder, closed at one end with a carbon plate, and at the other with a carbon crucible having a vent hole and a plate to form a receptacle for the zinc; they charged the cylinder with a mixture of oxide zinc ore and reducing carbon, and connected the carbon plates with the terminals of the current which flowed through the carbon of the charge and heated the latter above the reducing temperature of zinc oxide. The zinc vapor passed off through the vent hole in the crucible, the latter acted as condenser and collected the spelter.

Since then a great many electric furnaces have been constructed to recover zinc, especially from mixed sulphide ores which cannot be treated satisfactorily by a smelting process. All electric processes suffer from the fact that the cost is high, the extraction of metal low, and that of the zinc recovered a large part is obtained as oxide and has to be re-treated. With the exception of the DeLaval plant, which has at its disposal very cheap current, and perhaps the new Fulton furnace, electric smelting has been a commercial failure. The success of the treatment of mixed sulphide ores by roasting and leaching, followed by electrodeposition of zinc and smelting of residue, appears to have put a stop to electric smelting.

122. Examples of Electric Smelting.—A few examples are given to represent types of furnaces which have been tried on a working scale.

1. *DeLaval Process.*—The furnace, patented in 1903, is an indirect-heating arc furnace, in which the heat of the arc is transmitted to the charge by radiation and conduction. The furnace is an oblong refractory chamber which has a movable carbon electrode on each side, a charge hopper with screw feed on one end, a flue in the roof at the other, and a tap-hole on one side. The charge which forms a heap slanting from feed to flue-end, is heated by the arc; the ZnO is reduced by the C of the charge and Zn vaporized, the gangue is smelted, and the resulting slag tapped at intervals from a depressed hearth. The furnace is in operation at Sartsborg, Norway; the original furnace at Trollhättan, Sweden, having been replaced by one of the direct-arc-heating type which has one movable vertical carbon electrode in the roof, and a carbon block imbedded in the bottom of the furnace. Information regarding the workings of

¹*Eng. Min. J.*, 1885, XL, 92.

these two types of furnaces is practically confined to the report of Harbord.¹ The disadvantages of both furnaces appear to be a large production of blue powder; in fact, the first smelting is a concentration process which furnishes fused residue, some spelter, and mostly rich oxide; the oxide has to be re-treated, yielding spelter and again more or less oxide. The regular charge is given as 100 kg. roasted ore, 200 kg. oxide or powder, 25 kg. coke, and 5 kg. limestone. The resistance furnace holds about 3 tons charge and smelts in 24 hr. 2.8 tons ore; it averages 2,078 kw.-hr. per ton of ore, and 40.57 kg. electrodes; the arc furnace requires 70 per cent more energy and 25 per cent electrodes.

2. *Côte-Pierron Process*.²—In this process, patented in 1904, blende is decomposed by metallic iron, $\text{ZnS} + \text{Fe} = \text{Zn} + \text{FeS}$, in a combined resistance- and arc-heating furnace in which one electrode, movable, passes through the roof and another, fixed, forms part of the bottom. Decomposition of ZnS by Fe begins at $1,300^{\circ}\text{C}$.³ The charge is heated by resistance when the top electrode dips into the slag, and by the arc when this is not the case; resistance-heating furnishes the low temperature for the decomposition of PbS, arc-heating the high temperature for ZnS. The freezing-point curve ZnS-FeS of Friedrich⁴ covering a range from 0 to 60 per cent ZnS, shows that the components form an eutectic, 5 per cent ZnS + 95 per cent FeS, freezing at $1,188^{\circ}\text{C}$., and that ZnS is soluble in FeS to the extent of about 3 per cent. The furnace has on one side a vertical condensation chamber filled with coke from the bottom of which the spelter is tapped. Molten lead, matte, and slag are removed at intervals from the furnace. The process was put into operation at "Fonderies Electriques" near Pau, France, in 1907. In 1918,⁵ a new plant was started at Epierre. It has four furnaces, each treating 4 tons in 24 hr. The ore, averaging 35 per cent Zn, is mixed with C and CaO, CaO having a decomposing effect.⁶

3. *Imbert-Fitzgerald-Thomson Process*.—The Imbert process of 1907 resembles the one of Côte-Pierron in that it aims to decompose ZnS by means of Fe. Imbert found that a mixture of 1 part

¹ Abstract, *Eng. Min. J.*, 1912, XCIII, 314.

² Fleurville, *Electrochem. Met. Ind.*, 1909, VII, 468.

Haanel, *Bull. 3, Can. Dept. Mines, Mines Branch*, Ottawa, 1910.

Flusin, *Metall u. Erz*, 1918, XV, 147.

³ Eulenstein, *Metallurgie*, 1912, IX, 154.

⁴ *Metallurgie*, 1908, V, 114.

⁵ Flusin, *Met. Chem. Eng.*, 1918, XVIII, 17.

⁶ Brown-Oesterle, *Electrochem. Met. Ind.*, 1905, III, 378.

Fe_2O_3 and 3FeS forms a fluid bath at $1,000^\circ$ to $1,100^\circ\text{C}$. which dissolves 6 parts ZnS .¹ By the addition of molten iron, zinc is liberated and vaporized leaving behind slag and matte, of which the latter can be used again at least in part. Fitzgerald and Thomson constructed a resistor furnace for carrying on large scale experiments at the Hohenlohe Zinc Works, Silesia. The furnace is an oblong refractory chamber with arched roof made of carbon-resistor plates covered with a layer of magnesite to prevent oxidation of carbon and loss of heat. The current passing through the plates brought these to the temperature required to heat the furnace chamber. The results do not appear to have been satisfactory.

4. *Johnson Process*.²—A great deal of experimental work has been carried on to make this process an economic success, but it has been given up in the end.³ A mixed sulphide ore is roasted to eliminate most of the sulphur; the roasted ore is mixed with coal and heated in a retort to reduce Fe_2O_3 to Fe , as Fe_2O_3 has an oxidizing effect upon zinc vapor; the suitably prepared ore is smelted in a combined resistance- and arc-heating furnace provided with a duct for gas and vapor filled with carbon. The molten products, lead bullion, matte, and slag are tapped in the usual way; the zinc vapor rises in the duct and is collected in a condenser.

5. *Fulton Process*.⁴—In this process⁵ a direct-resistance-heating furnace is used. The charge, forming the resistor, is made up of briquettes consisting of a mixture of roasted calcined ore, ground coke and ground coal-tar pitch. The briquettes, 9 to 25 in. in diameter and 21 in. long and molded under a pressure of 500 to 1,000 lb. per square inch, are piled in three columns about 6 ft. high upon lower carbon terminals and their tops connected electrically; the briquettes of a pillar are cemented by a mixture of coal tar pitch and graphite. A cylindrical conductor carries the resistor charge. It can be raised and lowered by an hydraulic apparatus in a vertical

¹ Fitzgerald, *Tr. Am. Chem. Soc.*, 1911, XIX, 273; *Mines and Minerals*, 1911, XXXI, 703; *Met. Chem. Ind.*, 1911, IX, 259.

² *Electrochem. Met. Ind.*, 1907, V, 83; *Iron Age*, 1912, LXXXIX, 1082; *Met. Chem. Eng.*, 1912, X, 281, 537, 1913, XI, 582, 1917, XVI, 375, XVII, 126; *Eng. Min. J.*, 1913, XCVI, 965, 1157; *Tr. Can. Min. Inst.*, 1914, XVII, 107; *Min. World*, 1914, XL, 48.

³ The American Smelting & Refining Co. has acquired the Johnson patents and intends to do experimental work at its zinc plant in Pueblo, Colo.

⁴ *Met. Chem. Eng.*, 1917, XVI, 158; 1918, XVIII, 539; *Tr. A. I. M. E.*, 1920, LXIV, 188.

⁵ U. S. Patent No. 1,213,180, Jan. 23, 1917.

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retort which forms the upper part of the furnace. In working, the resistor charge is raised that it may be inclosed by the retort, and a 3-phase alternating current turned on. At first the temperature in the retort is maintained at from 600 to 700°C. to expel water, vapor and hydrocarbons; these descend and pass through the lower electrode into the condenser and leave the latter through a vent in the bottom. The temperature is then raised to the reduction and distillation temperatures, when zinc vapor collects in the condenser to be tapped at intervals, and carbon monoxide passes off through the bottom vent. A charge of 12 briquette columns, each weighing about 600 lbs. and containing about 20 per cent Zn, is treated in 6 hr. The process is still in its experimental stage.

CHAPTER VIII

ELECTROLYSIS OF ZINC ORES

123. General.¹—Electrolysis of zinc ores embodies, broadly speaking, two steps, preparation of a zinc solution and deposition of zinc from that solution. It is too expensive to be applied to pure zinc ores, hence its field is limited to mixed ores, such as lead- and copper-zinc sulphides from which the metals cannot be recovered by smelting. Even with these ores the cost of treatment appears to be so high, \$12 to \$20 a ton, that the residue remaining after the extraction of zinc must have considerable value, contain *e.g.*, precious metals, to help pay expenses, if any profit is to result from the operation.

This opinion, which is generally held, has been changed in recent years by the experience gained in large works to the conviction that electrolysis of pure zinc ores cannot only compete with smelting but will replace it in the not far distant future. Some of the reasons are, that roasting pure zinc ores is cheaper than complex ores; that while the cost of leaching is nearly proportional to the soluble zinc content—settlement, filtration, purifications costs are very much lower; that electrolyzing costs being proportional to the amount of zinc plated out, electrolysis will be cheaper as very little zinc has to be returned to the process for purifying the electrolyte, *e.g.*, at Great Falls 8 per cent of the zinc deposited; that the small amount of insoluble residue if valueless (as in Missouri blende) can be freed from zinc solution by counter-current washing, not needing filtering, and the residue run to waste; that the purification practically nil, filtration is unnecessary, as also treatment of residue; that the yield of zinc is high, *e.g.*, with Missouri concentrates 94 per cent. In general, the coal required to produce a ton of zinc from a 50-per cent concentrate will also produce electric energy necessary

¹ Günther, E., "Die Darstellung des Zinks auf Elektrolytischem Wege," Knapp, Halle, 1904.

Ralston, O. C. *Electrolytic and Deposition Hydrometallurgy of Zinc*. McGraw-Hill Book Co., Inc., N. Y., 1921.

Engelhardt-Huth, *Metallurgie*, 1910, VII, 1.

Engelhardt, *Metallurgie*, 1913, X, 60.

Matthewson, *Bibliography*, *Tr. Can. Min. Inst.*, 1917, XX, 137.

to deposit this amount of zinc from sulphate solution; the difference in cost of plant will not be sufficiently great to affect materially the cost of treatment; the number of men required is one-third that of smelting; and the yield and quality of metal are higher.

Siebenthal¹ enumerates 10 electrolytic plants existing in the United States in 1915 as seen in Table 40.

TABLE 40.—ELECTROLYTIC ZINC PLANTS OF U. S. IN 1915

Company	Location of plant	Daily spelter capacity	Remarks
American Smelting & Refining Co.	Omaha, Neb.	Experimental	Operated in 1915.
American Smelting & Refining Co.	Murray, Utah	Experimental	
Anaconda Copper Mining Co.	Anaconda, Mont.	25 tons	Under construction; 10 tons operated in 1915.*
Anaconda Copper Mining Co.	Great Falls, Mont.	100 tons	Under construction.
Bully Hill Copper Co.....	Bully Hill, Cal.	Experimental, 10 tons	Operated in 1915. Under construction.
Colorado Metal Mining & Reduction Co.	Georgetown, Colo.	Ore capacity, 100 tons	Mal m process; under construction.
Electrolytic Zinc Co.....	Baltimore, Md.	10 tons	Under construction in 1915; now in operation.
Judge Mining and Smelting Co.	Park City, Utah	15 tons	Under construction.
Mammoth Copper Mining Co.	Kennett, Cal.	Experimental, 25 tons	Operated in 1915. Under construction.
Northwestern Metals Co....	Helena, Mont.	Ore capacity, 100 tons	Mal m process; completed 1914; never operated.
Reed Zinc Co.....	Palo Alto, Cal.	Experimental	Operated in 1914-15.
River Smelting & Refining Co.	Keokuk, Iowa	Experimental	Operated in 1915.

* Twenty-five tons, May to November, 1916, when it was closed down. The Great Falls plant was put into operation in September, 1916, had a capacity of 100 tons spelter, December, 1916; it was enlarged to 150 tons in 1918.

Of these only two, *i.e.*, Great Falls, Mont., and Park City, Utah, are producing electrolytic spelter; both have water power.

The plant at Trail, B. C., which started in 1916, is the third plant of the continent. All these plants use a sulphate electrolyte.²

¹ *Min. Res. U. S.*, 1915, Part I, 945.

² Létrange, English Patent No. 3,211, July 22, 1881; U. S. Patent No. 286,208, Oct. 9, 1883.

The electrolytes can be either aqueous or igneous solutions; the latter, represented by the Borchers, Swinburne and Ashcroft, Schultze processes, either have not gone beyond the laboratory stage or are obsolete, and need not be considered. The aqueous solutions tried are sulphate, chloride, and caustic. The last (Kiliani) has fallen into disuse; with the exception of the Brunner Mond works in England employing chloride solution (§136), all operating plants use a sulphate electrolyte and an insoluble sheet-lead anode, and a sheet-aluminum cathode. Roasting of blende and electrolysis of sulphate solution is taken up in detail; electrolysis of chloride solution with the Höpfner process, which was in use at Führfort, Germany, and is doing regular work at Winnington, England, is outlined.

124. Deposition of Zinc from Sulphate Solution.¹—In a slightly acid solution of ZnSO_4 the salt is largely dissociated into Zn^{++} and SO_4^{--} ions. In electrolyzing the solution with an insoluble anode the Zn^{++} ions migrate to the cathode, give up their charges to the cathode, and are deposited as metallic zinc; similarly the SO_4^{--} ions migrate to the anode, give up their charges to the anode, and decomposing H_2O form H_2SO_4 and O . The decomposition voltage of ZnSO_4 is 2.35, that of H_2SO_4 is 1.67. In works the pressure per tank with electrodes in parallel is 3.5 volts.² The electrochemical equivalent of Zn is 0.33873, or 1.2194 g. Zn are deposited per ampere-hour, which is equal to 2.68 lb. per thousand ampere hour. The electric conductivity of solutions of ZnSO_4 has been given in Table 13.

One of the principal difficulties encountered in electrolysis is the formation of a spongy zinc deposit which cannot be liquefied by melting owing to its tendency to oxidize. The leading factors which determine the character of the deposit are temperature, current density, concentration of zinc and acid in electrolyte, and presence

¹ Ingalls, *Eng. Min. J.*, 1916, ci, 425.

Hansen, *Met. Chem. Eng.*, 1916, xiv, 120.

Hall, *Tr. A. I. M. E.*, 1917, lvii, 702.

French, *Met. Chem. Eng.*, 1917, xvii, 647.

Laboratory Tests, *Bull. Mo. Sch. Mines & Met.*, 1917, iv, No. 1.

Hansen, *Tr. A. I. M. E.*, 1919, lx, 206.

Broughton, *Chem. Met. Eng.*, 1919, xx, 155.

Hanley, *Min. Sci. Press*, 1920, cxxi, 795.

Laist-Frick-Elton-Caples, *Tr. A. I. M. E.*, 1920, lxiv, 699.

² With 25 amp. per square foot of cathode surface, 8 per cent acid and 2-in. spacing, it is nearer 3.4 than 3.5 volts.

of impurities. Many investigations have been carried on to solve the problem as *e.g.*, by Kiliani¹ Nahnsen,² Mylius and Fromm,³ Hasse⁴ and others. Table 41 gives the results of Nahnsen dealing with the

TABLE 41.—EFFECTS OF TIME AND TEMPERATURE ON CHARACTER OF ZINC DEPOSIT

Current density, amperes per square foot	Temperature of electrolyte, degrees Centigrade			
	1	10	20	30
Character of deposit				
0.93	firm	spongy	spongy	
4.57	firm	spongy at first	spongy	
9.13	firm	firm	spongy at first	spongy
13.60		firm	firm	spongy at first
18.20		firm	firm	firm

effects of temperature and current density of electrolyte upon the character of the deposit. They indicate that a high current density favors a firm deposit, be the temperature high or low, and that as the density is decreased the temperature has to be lowered; in fact, low densities produce high temperatures, and high temperatures increase corrosion, which doubles with every 22°C., and decrease current efficiency. The equilibrium between cell temperature and dissipation of heat by evaporation, radiation, convection, etc., varies with the current densities. In order to prevent rise of temperature above 50°C., tanks have cooling coils. A current density of 20 to 25 amp. per square foot cathode area and a temperature of 40° to 50°C. are common in plants. Pring and Tainton⁵ propose to use an electrolyte rich in zinc (140 g. per liter) and free acid (75 g. per liter) and a current density ranging from 50 to 300, preferably from 140 to 150 amp. per square foot; the high zinc content is to be reduced to the starting concentration of ordinary electrolysis and a pure deposit to be obtained.

¹ *Berg. Hüttenm. Z.*, 1883, XLVII, 250.

² *Op. cit.*, 1891, L, 393.

³ *Zt. anorg. Chem.*, 1895, IX, 144.

⁴ *Zt. B. H. u. S. W. i. Pr.*, 1897, XLV, 327.

⁵ *J. Chem. Soc.*, 1914, CV¹, 710.

Smith, *Tr. A. I. M. E.*, 1920, LXIV, 754.

At Martinez, Cal.,¹ the Central Mining Co. of London has in operation a plant with a daily production of 6 tons spelter. The electrolyte contains from 22 to 27 per cent free acid, about 70 g. zinc per liter on entering a vat and 30 g. on leaving. Of the impurities, Sb gives much trouble, Co and As have been run to the extent of 30 mg. per liter without causing inconvenience. The current density is 100 amp. per square foot, the voltage per cell is 4; the current efficiency is about 89 per cent, about 1.77 kw.-hr. is consumed per pound of zinc produced.

Butters² treats roasted blende magnetically, attacks the magnetic part with concentrated solution which decomposes ferrite, and turns the solution onto the non-magnetic part.

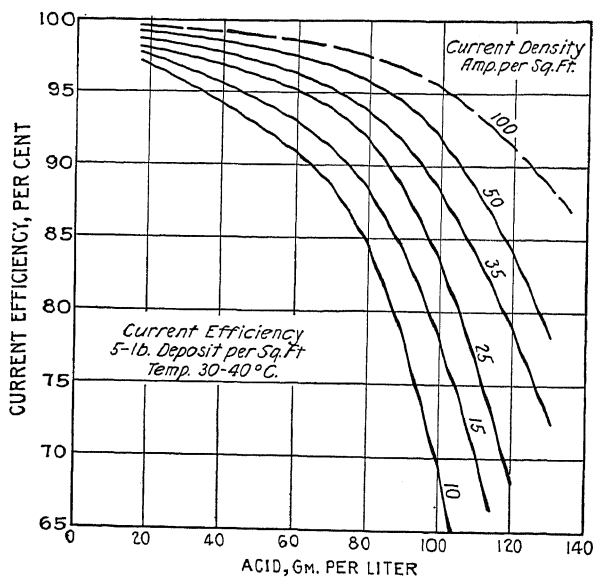


FIG. 185.—Fall in current efficiency with increase of acid.

The concentration of the neutral solution is moderate, entering a vat it contains about 100 g. Zn per liter and on leaving 35 g. Zn and 10 to 12 per cent free acid. The acidity of the starting solution is low, 150 g. H_2SO_4 per liter. As Zn is more electro positive than H, H_2SO_4 is decomposed before $ZnSO_4$, and Zn will come down only

¹ Editor, *Eng. Min. J.* 1921, CXI, 342.

Bosqui, *ibid.*, p. 456.

² Bullock, *Tr. A. I. M. E.*, 1920, LXIV, 753.

when an overvoltage of 0.77 will have been reached. The larger the content of free acid, the more H will be set free and the lower the current efficiency; the greater also will be the corrosion of the cathode zinc which increases with the temperature. Some free acid may be necessary to prevent the formation of basic salts near the anode. On leaving a vat the content of free acid will have increased to 11 per cent.

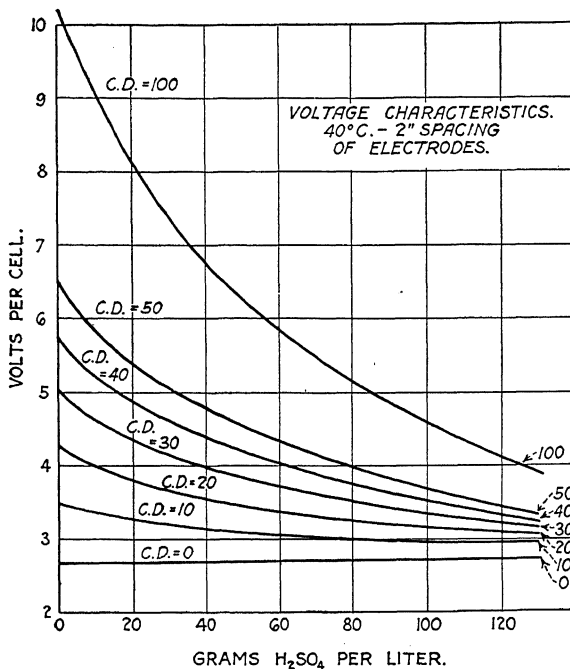


FIG. 186.—Fall in voltage with increase of acid.

The fall in current efficiency and in voltage with increase of free acid in a working solution using different current densities are shown in Fig. 185 and 186.¹ Figures 187 to 191 give results of the investigations by Laist-Frick-Elton-Caples² made with a prepared neutral solution containing in grams per liter: Zn 110.0, Mn 1.6, Cu 0.001, Cd 0.002, Fe trace, H_2SO_4 0.0. Figure 187 shows that as the acid-content of the electrolyte increases and the zinc-content decreases, the ampere efficiency decreases. Figures 188 and 189 show how

¹ Hansen, *Tr. A. I. M. E.*, LX, 217-219.

² *Tr. A. I. M. E.*, 1920, LXIV, 699.

with a constant acidity at 20 and 50 amp. per square foot, the voltage decreases with rise of temperature, which fall is less marked with high percentages of acid than with low; or the decrease in voltage due to increase in temperature of the electrolyte is greater the higher the current density and the lower the acid content, the effect becoming less pronounced as the temperature increases. Figure 190 shows

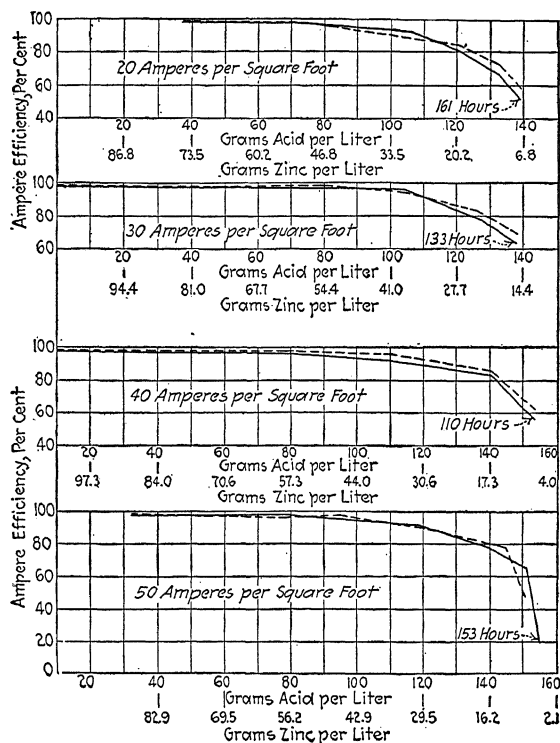


FIG. 187.—Effect of time of deposition and ratio of acid to zinc content of electrolyte on ampere efficiency. Dotted line is plotted from 8-hr. deposits; solid line is for continuous deposition for hours indicated at end of line.

the effect of increasing temperature of electrolyte on voltage required at various current densities and ratios of acid to zinc content of solution. The decrease in ampere efficiency is not so noticeable with pure as with impure solutions. Figure 191 shows the effect of temperature between 25 and 45°C., and acidity between 0 and 13 per cent, on the resistance of the electrolyte at 50 amp. and 20 amp. per square foot at 4-in. spacing center-to-center anodes. It is nearly as economical, assuming equal ampere efficiency, to operate

at 50 amp. per square foot and 65°C. with 13 per cent acid, as to use 20 amp. sq. ft. at 25°C. with 13 per cent acid. An increase in either

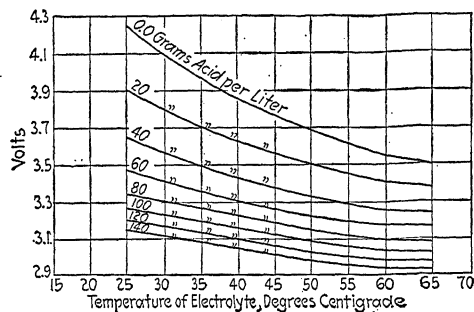


FIG. 188.—Effect of temperature on resistance of electrolyte at 20 amperes per square foot.

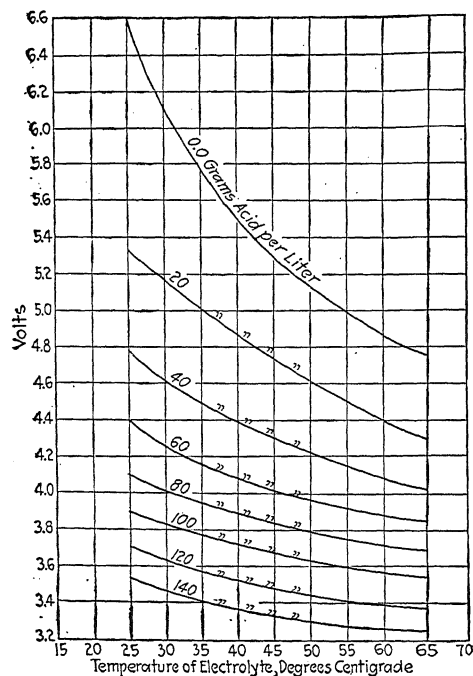


FIG. 189.—Effect of temperature on resistance of electrolyte at 50 amperes per square foot.

temperature or acidity brings the voltages required for different current densities closer together.

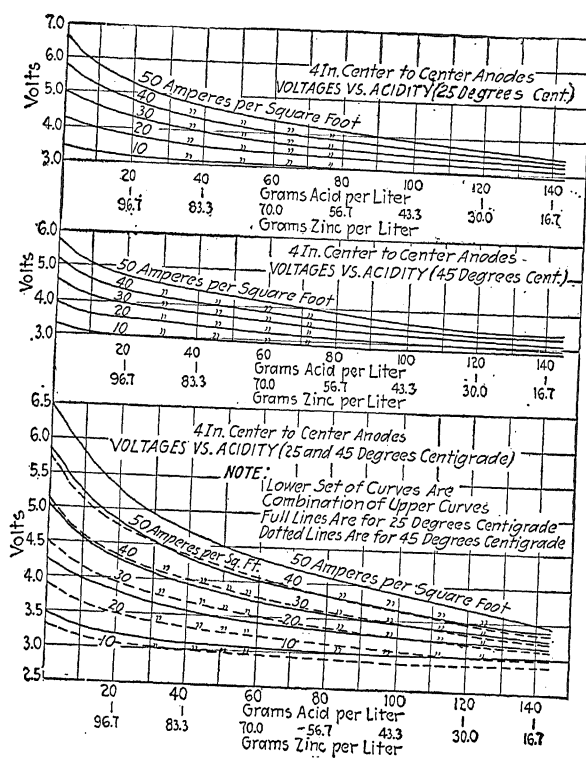


FIG. 190.—Effect of temperature and acidity on resistance of electrolyte for varying current densities.

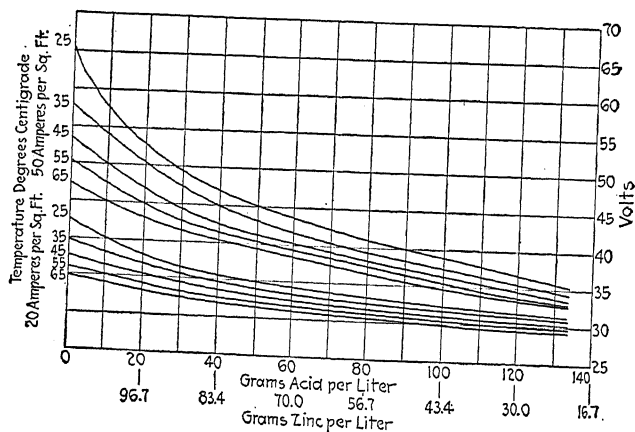


FIG. 191.—Effect of temperature and acidity on resistance of electrolyte at 50 amp. and 20 amp. per sq. ft. of 4-in. spacing center to center anodes.

The power requirements kilowatt-hour for the deposition of 2,000 lb. cathode zinc with a 5-lb. deposit per square foot of cathode in a working solution of 30 to 40°C., with different current densities and increasing acid contents, as plotted by Hansen¹ are shown in Fig. 192.

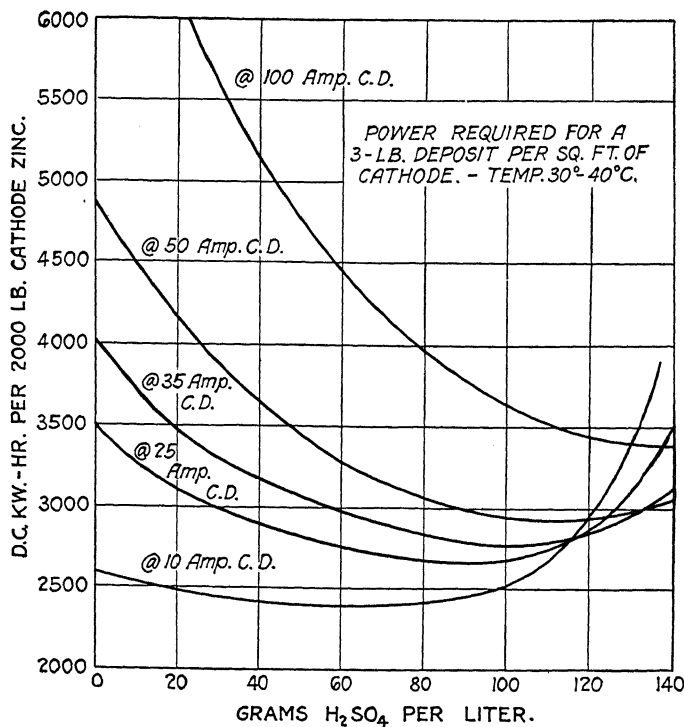


FIG. 192.—Power required for a 3-lb. deposit per sq. ft. of cathode area.

The actual power consumed in the production of metallic zinc is about 1.5 kw-hr. per pound of zinc in the electrolytic tanks.²

The data regarding power consumption of Laist-Frick-Elton-Caples³ are given in Figs. 193 and 194. These show the relations of power efficiency to variations in current density, zinc content, and ampere efficiency, although the voltage required decreases steadily with the increase of acidity; the figures show that the ampere

¹ *Tr. A. I. M. E.*, 1919, LX, 221.

² Hall, *Tr. A. I. M. E.*, 1917, LVII, 716.

³ *Tr. A. I. M. E.*, 1920, LXIV, 699.

efficiency falls rapidly after the acid to zinc ratio increases above a certain point, and the power efficiency also falls as the drop in ampere efficiency is too rapid to be made up by the decrease in voltage from increased acidity.

Clevenger and Mulock¹ have given a graphical representation of the relationship existing between the principal electrical data,

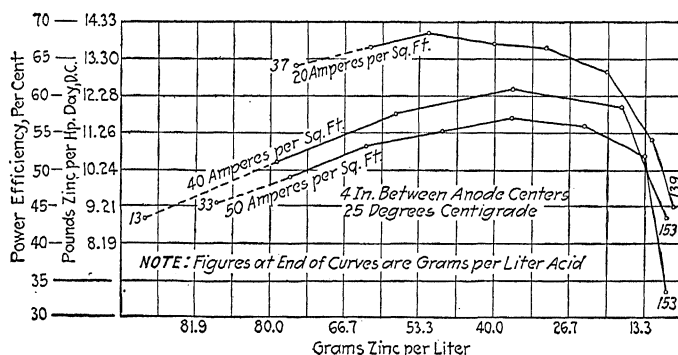


FIG. 193.—Relation of power efficiency to variations in current density, acidity, and ampere efficiency.

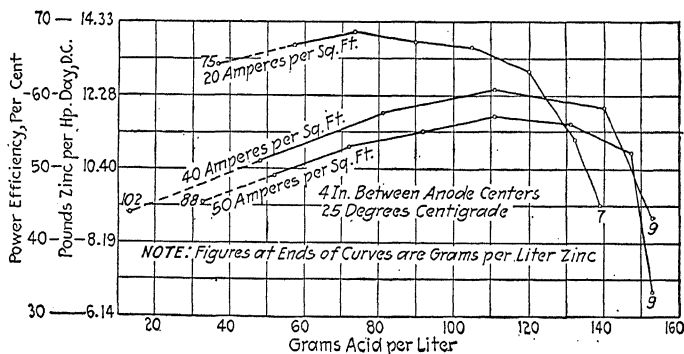


FIG. 194.—Relation of power efficiency to variations in current density, zinc content, and ampere efficiency.

including amount and cost of production, for the electrodeposition of zinc in a modern plant.

Impurities electro-negative to zinc ought to be absent in the electrolyte, as they are likely to cause the formation of spongy zinc and to affect unfavorably the current efficiency. As zinc is the most electropositive of the common metals found in a zinc solution, this

¹ Chem. & Met. Eng., 1919, xx, Supplement.

has to be purified before it is electrolyzed. In fact, success in electrolysis has been obtained only, since the attention necessary has been given to purification.¹

Pure zinc is soluble with difficulty in sulphuric acid, and impure zinc is fifty times as soluble. As any impurity in the electrolyte which is precipitated on a cathode favors resolution of zinc, it has to be removed before electrolysis can proceed. With sufficient impurity, re-solution might offset the depositing power of the current, no zinc would be produced, and only hydrogen generated at the cathode and oxygen at the anode. With small amounts of impurity, the cathodes would be more or less corroded and be full of shot holes of various sizes, and the current efficiency greatly reduced. It is to be noted that the harmful effects of impurities are cumulative; in the presence of a small amount of copper, the deleterious effect of a little arsenic or antimony is greatly intensified. The only safe way of operating is to remove impurities completely.

Hansen² divides the impurities into non-cumulative and cumulative.

The non-cumulative impurities are Cu, Cd, As, Sb, Fe, Mn, SiO₂, Al₂O₃.

Copper and *Cadmium* are precipitated with zinc in the early cells of a cascade and affect the deposit, unless as is common, fresh solution is fed into all cells of a cascade; the current efficiency in these cells will therefore be reduced, this is less the case with Cd than with Cu; the Cd-content ought not to exceed 20 mg. per liter, the Cu-content 10 mg. Cadmium to the extent of 0.6 g. per liter does not injure the current efficiency nor the character of the deposit, but if highest-grade spelter is to be produced, it ought not to exceed 20 mg. per liter. In larger amounts of copper than 10 mg., holes are eaten through the cathodes leaving a black deposit on the aluminum surface.

Cadmium and copper are precipitated from an alkaline electrolyte by zinc dust, copper more readily than cadmium as seen by the curve of Hanley³ given in Fig. 195. The same rate of precipitation is shown in Fig. 213.

Arsenic and *Antimony* are not precipitated, but reduce the current efficiency, less so in the absence than in the presence of manganese; in the latter case 0.00032 to 0.001 g. As or Sb reduces the current

¹ Field, *British Association*, October, 1920; *Min. Mag.*, 1920, XXIII, 248.

² *Tr. A. I. M. E.*, 1916, 22.

³ *Min. Sci. Press*, 1920, CXXI, 794.

efficiency to such a degree as to make electrolysis impossible. Both are readily precipitated in the presence of ferric iron as $\text{Fe}_2\text{As}_3\text{O}_4$ and $\text{Fe}_2\text{Sb}_3\text{O}_4$ (?) with limestone and calcine, also small amounts of Pb, provided the iron in solution is thoroughly oxidized. Iron is maintained in the ferric state if manganese is present; if the solution does not contain sufficient iron or manganese, these have to be added as ferric or manganic oxide or salt. Precipitation of As by H_2S has been proposed by Hanley (*Chem. Met. Eng.*, 1921, xxiv, 693).

Iron is not precipitated, but it reduces the current efficiency. It was thought that FeSO_4 oxidized at the anode to $\text{Fe}_2(\text{SO}_4)_3$ might be reduced by the H adhering to the cathode and thus act as a depo-

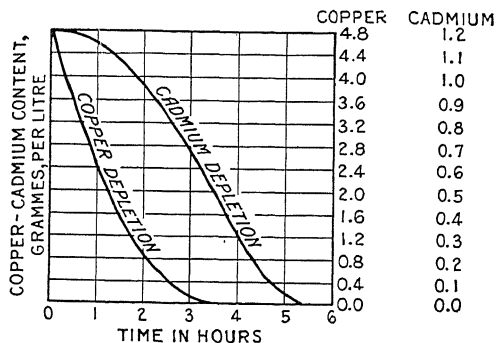


FIG. 195.—Relative rates of precipitation by zinc of copper and cadmium.

larizer, but unfortunately $\text{Fe}_2(\text{SO}_4)_3$ dissolves Zn to such an extent that the advantage of the removal of H is more than neutralized.

Manganese alone is harmless; however, MnSO_4 is in part oxidized at the anode by the liberated O to HMnO_4 according to $2\text{MnSO}_4 + 2\text{O} + 6\text{H}_2\text{O} = 2\text{HMnO}_4 + 2\text{H}_2\text{SO}_4$, and this reacts according to $2\text{HMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + 3\text{H}_2\text{SO}_4$, quickly in hot neutral or basic solution, and slowly in cold acid; further MnO_2 assists in the oxidation of FeSO_4 according to $2\text{FeSO}_4 + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + 2\text{H}_2\text{O}$. With the low acid concentration, MnO_2 adheres to the anode and has to be scraped off; with the high it drops as a slime to the bottom of the vat and contains substantially the same amount of PbO_2 . An analysis of such slime gave MnO_2 68.0, Pb 13.7, Zn 1.2 per cent; the loss of lead anode amounted to 6.9 lb. per ton of cathode zinc made.

The cumulative impurities are alkali, and Mg; further Ni, Co, Va, and perhaps Ur; to which should be added Cl.

Alkali metals and *Mg* have no important bearing upon the process.

Nickel, Cobalt, Vanadium, Uranium.—These metals are not plated out, but affect the cathode deposit and reduce the current efficiency, and this the more the greater the amount of free acid. Cobalt has been found to be especially harmful. Gepp and Clevenger found 0.15 mg. per liter to be fatal, 0.10 mg. seriously impairing electrolysis. Cobalt can be precipitated in the presence of manganese, from a neutral solution by potassium permanganate¹ or by adding β -naphthol, NaNO_2 , and acid, when nitro- β -naphthol is formed which precipitates cobalt (Clevenger); or by zinc dust from a neutral solution, preferably warm ($75^\circ\text{C}.$), in the presence of ferric iron, copper and arsenic, or only of copper and arsenic;² in the latter case 12 to 15 parts Zn and 1.5 parts dissolved As and Cu being added for 1 part Co.

Chlorine compounds have to be absent, as if present to the extent of 50 mg. per liter the Cl liberated at the anode attacks this readily. A method of freeing an electrolyte from chlorine is the addition of a silver salt. In case this is not feasible the lead anode may have to be replaced by one of corroded iron; usually the water is sufficiently free from Cl to make precautions unnecessary.

Nitrates are undesirable as regards anode corrosion, especially in the presence of Cl.

Foul solutions are improved by the use of organic addition agents,³ such as glue, lanoline, especially eikonogen, pyrogallol, beta-naphthol, *e.g.*, 1 g. per liter,⁴ in that they increase current efficiency and have a beneficent effect upon the deposit. Glue is the most trustworthy agent, and the cheapest; there is used 0.5 to 1.5 oz. glue per ton of metal produced. Too much glue causes brittle metal and starts resolution.

Other methods of purifying solution are to draw off parts of solutions and bring them up to standard; or to cut off some current and maintain the feed unchanged whereby acid concentration and temperature are diminished, and consequently corrosion is reduced. These, however, are only make-shifts because anything that tends to decrease the acidity must be paid for in an increased power bill. All solutions should be purified before going into the tank room.

¹ G. H. Clevenger, British Patent No. 115,846 and 115,847, May 7, 1918; U. S. Patent No. 1,283,077 and 1,283,078, Oct. 29, 1919.

² Electrolytic Zinc Co. of Australia Proprietary, British Patent No. 126,296, Apr. 18, 1919.

³ Mazzucchelli, *Chem. Abstr.*, 1915, IX, 1719.

⁴ Watts-Shape, *Tr. Am. Electrochem. Soc.*, 1914, XXV, 291.

All plants use cast lead anodes and sheet aluminum cathodes. The anode which has to be pure lead (chemical lead), becomes quickly coated with a layer of MnO_2 and PbO_2 ; it is not attacked if the electrolyte is free from chlorides. The sheet aluminum cathode was adopted after starting sheets of zinc had proved unsatisfactory on account of buckling and consequent short circuiting, of re-solution of zinc from the back, and of cost of making. In order to obtain good adherence of deposited zinc to the aluminum plate, and thus good electric contact and prevention of re-solution of the zinc, the aluminum plate has to be roughened. With a current density of 22 to 25 amp. per square foot it is customary to strip the zinc deposits every 48 hr.; 72-hr. sheets are made sometimes, but the danger of buckling of the deposit and the consequent re-solution, and of short circuiting through sprouting have proved less advantageous than the 48-hr. cathodes, as the better current efficiency attained more than balances the higher cost of the more frequent stripping. The cathodes are provided with grooved strips of wood on the sides to prevent excrescences at the edges and to facilitate the stripping of deposited zinc.

The circulation of the electrolyte need not be rapid, *e.g.*, 100 tons per hour for 720 tanks, as with the current density of 22 to 25 amperes the evolution of gas is sufficient to provide for the necessary agitation.

The temperature of the electrolyte helps the corrosive influence of impurities, hence cooling coils are required to keep the temperature at about 50°C .

The electrolyte is little fouled, as the aim is to remove all impurities before any zinc is deposited.

125. Outline of Process.—The electrolysis of zinc ores from sulphate solutions embodies the following operations: Roasting, leaching, separation of solution from residue, purification of solution, and electrolysis, melting of cathode, and treatment of residues. Only the general features will be taken up here, the details are reserved for the descriptions of three plants, those at Great Falls, Montana, (§132), Trail, B. C. (§133), and Park City, Utah (§134).

126. Roasting.—The object of roasting blende concentrates is to decompose ZnS into ZnSO_4 and ZnO , which are soluble in H_2O and dilute H_2SO_4 respectively, and to oxidize the associated sulphides. The process is therefore a combination of sulphatizing and oxidizing roasts. The conversion of ZnS into ZnSO_4 is a very slow and unsatisfactory operation, conversion into ZnO is much

quicker and gives better results; the former must try to oxidize iron sulphides before the temperature rises sufficiently to attack the blende; in order to make this possible an abundance of air is required. It has been found in the electrodeposition of zinc with insoluble anodes from sulphate solution that as long as the roasted ore contains from 3 to 4 per cent water-soluble ZnSO_4 , enough H_2SO_4 is generated by electrolysis to replenish loss of H_2SO_4 in the treatment of the ore. The roast therefore differs from the treatment of blende that is to be smelted. The temperature has to be lower, as ZnSO_4 is rapidly converted at 720°C . (§27) into $3\text{ZnO}\cdot 2\text{SO}_3$, and this salt at 767°C . into ZnO ; in addition it has been found that if roasting is too rapid and the temperature exceeds 700°C ., a considerable portion of the ZnO is likely to combine with the Fe_2O_3 which is always present, and form $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ insoluble in dilute H_2SO_4 . Usually the roasting temperature is not allowed to exceed 700°C ., more frequently it is held at 650° . In roasting within limits of temperature, the time given and the need of keeping the ore porous, there will remain in the ore a considerable portion of undecomposed sulphide; the coarser the ore the longer will it take for the roast to penetrate the individual particles; the more frequent the rabbling the more effective will be the roast, fine ores can thus be fed more quickly than coarse.

The McDougall type of furnace is the one used in this country. It differs from the furnace used in roasting sulphide copper ore in that the last two hearths are heated from fireplaces to assist in the oxidation of undecomposed sulphide and decomposition of sulphate. The McDougall-Wedge roaster, which is used in the three electrolytic plants of the country, is shown in Fig. 196. It has the well-known characteristics of the Wedge furnace for roasting pyrite and sulphide copper ore.¹ These are a central accessible air-cooled driving shaft, 5 ft. in diameter, which without bottom step runs on roller bearings; several water-cooled rabble-arms which are removable through the central shaft; and a mechanically stirred drying hearth for wet concentrates which forms the roof of the top roasting hearth. The furnace is 25 ft. in diameter outside, and has seven roasting hearths; it is provided with two fireplaces placed opposite one another, both shown in vertical section, one in part-elevation. The hot fuel gases from a fireplace pass through adjustable ports in the sixth and seventh roasting hearths and travel upward in a direction opposite to that of the ore; the mixture of fuel

¹ Hofman, "Copper," 1918, p. 112.

and sulphurous gas is withdrawn from the first and second roasting hearths through ports provided with dampers. On hearths 2, 4, 6, there are provided special drop-holes besides the central discharge opening. This arrangement permits the ore to descend in the drop-holes and the gas to ascend in the central annular spaces between shaft and hearths; the amount of flue dust formed is thus greatly diminished. The arms on hearths 1, 2, 3, 4, 5, are air-

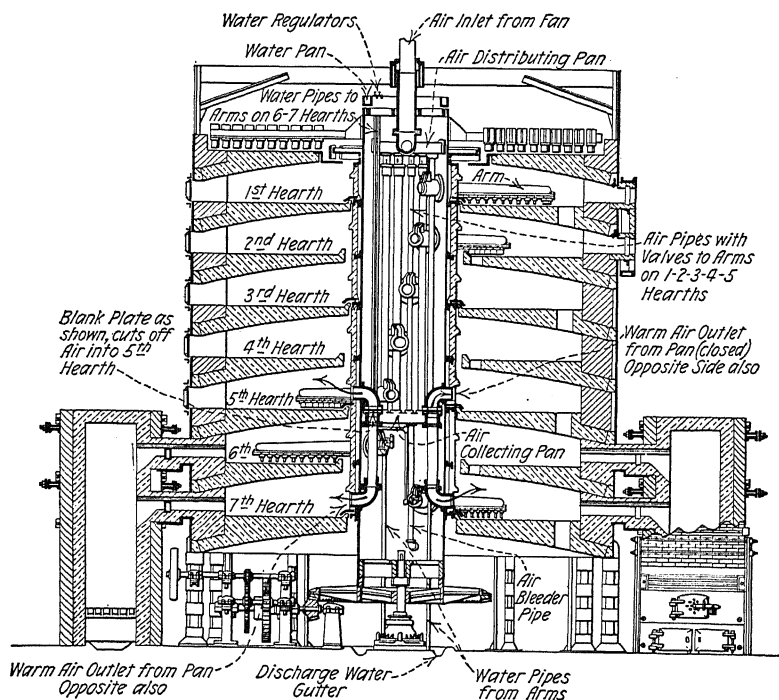


FIG. 196.—Wedge roaster.

cooled, those on hearths 6 and 7 are water-cooled. Air from a fan is delivered through a vertical pipe in the center of the shaft to a distributing pan; from this it enters the several arms through valves which can be regulated from the top. The warmed air is assembled in a collecting pan, and delivered on to the sixth and seventh hearths. The drawing shows that the delivery of warmed air on to the fifth hearth is cut off by a blank plate. At the top of the central shaft is a water pan, from which pass downward water pipes for the rabbling arms on the sixth and seventh hearths;

the outflow from these arms is collected in the discharge-water gutter. The work of this furnace is discussed in §§132, 133, 134.

Another furnace of the Wedge Mechanical Furnace Co. (Greenwich Point, Philadelphia) is in use in some Eastern plants which use the sulphurous gas for the manufacture of sulphuric acid; it keeps separate the fuel and sulphurous gases, the former being withdrawn through down-draft in a separate flue.

The effects of size of particles and of temperature have been studied in the laboratory by Hansen¹ on table and flotation con-

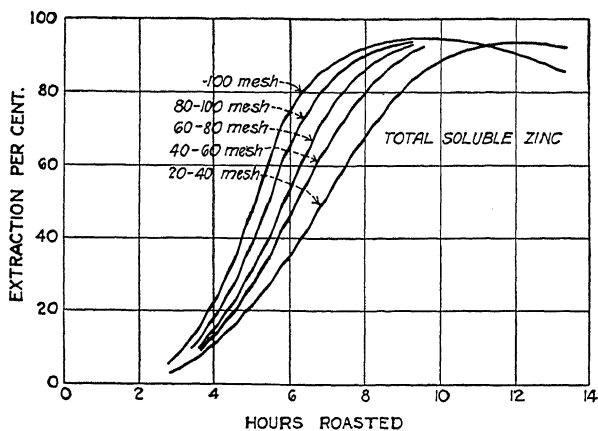


FIG. 197.—Daly-Judge concentrates roasted at 650°C. Effect of size and time on solubility of zinc.

centrates of the Daly-Judge Mining & Smelting Co., Park City, Utah, which are a mixture of crystals of pure blende, pyrite, galena, and contain Zn 47.70, Cu 1.12, Fe 4.50, S 27.00, Cd 0.31, Pb 2.19, SiO₂ 6.70, CaO 4.95, Al₂O₃ 1.80, MnO 0.67 per cent, Ag 12.20 and Au 0.02 oz. per ton. Figure 197 represents the effects of size and of time on solubility of zinc; it shows that in the finer particles the zinc is rendered soluble in larger quantity and in less time than the coarser; also that the prolongation of the roast over the necessary time diminishes the solubility, and that this is more noticeable in the finer than the coarser sizes, 100-mesh vs. 20-40-mesh. It would seem that 60-mesh is the proper size.

Figure 198 shows the effects, temperature and time have upon the solubility of zinc. At 550°C. the water-soluble and total-soluble zinc proceed evenly and are satisfactory provided enough

¹ Bull. A. I. M. E., No. 152, August, 1919.

time is given to the operation, 32 hr.; at 600° the water-soluble zinc is smaller, but the total-soluble zinc is greater than at 550°, and the result is obtained in less time, 24 hr.; at 650° the maximum of total-soluble zinc is obtained in 12 hr., prolongation of the roast causes a falling-off of soluble zinc. This shows that 650°C. and 10 or 12 hr. give a satisfactory extraction.

The data of Hansen¹ with a Wedge roaster at 740°C. and a uniform feed of 24 tons in 24 hr., varying the speed of the rabble arms from 260 sec. per revolution to 150 sec., and thereby diminishing the time given to roasting from 10 hr. to 6.9 and 5.75 hr., are of interest. The furnace is 25 ft. outside and 21 ft. inside diameter;

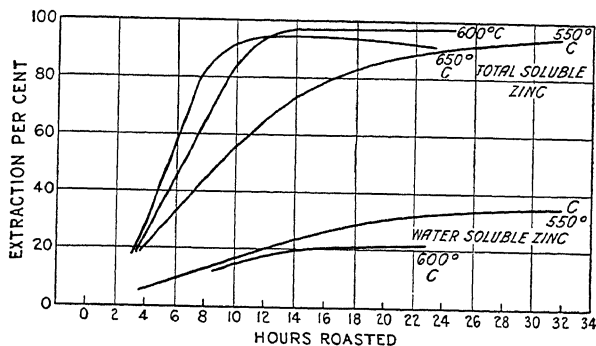


FIG. 198.—Daly-Judge concentrates roasted at given temperatures.

has seven roasting hearths with 2,350 sq. ft. hearth area; two rabble-arms each with 10 blades to a hearth, the arms of the five upper hearths are air-cooled, the warmed air being discharged on to the sixth and seventh hearths, the arms of the two lower hearths water-cooled; there are two coal-fired combustion chambers at opposite points with flues leading on to the sixth and seventh hearths. The ore treated is a blende concentrate made up of +40-mesh, 27 per cent; 40-60-mesh, 24.4; 60-80-mesh, 16.2; 80-100-mesh, 7.8; and -100-mesh, 23.1 per cent. The chemical analysis gives Zn 34.80, Cu 0.40, Fe 15.50, Mn 0.30, Pb 2.70, S 34.80, SiO₂ 4.70, CaO 1.15 per cent. Figure 199 represents the effects of variations of speed of rabbles. Slowing down the rabble-shaft decreases the rabbling rate and thereby raises the thickness of the ore-bed on the hearth. The result is a lessening in the rate of oxidation, but the end result, elimination of S and solubility of Zn is about the same with a 10-hr. roast as with one that lasts 5.75 hr.

¹ Loc. cit.

The effect of temperature in a Wedge roaster on Sullivan ore at Trail, B. C., is shown by Hamilton, Murray, and McIntosh.¹ The ore, of which 70 per cent passes a 200-mesh screen, has the composition Pb 13.2, Fe 25.3, SiO₂ 2.4, Al₂O₃ 2.9, CaO 1.4, S 28.5, and Zn 6 per cent. The results are given in Table 42 and the effects of

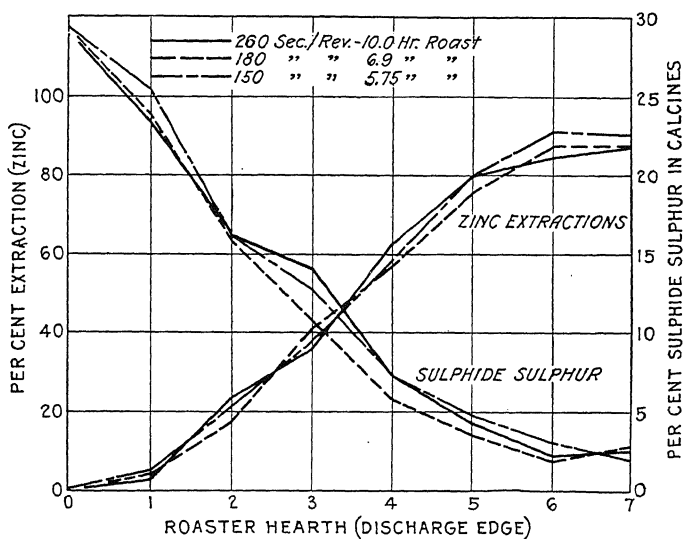


FIG. 199.—Daly-Judge concentrates; Wedge roaster temperature 740°C.; feed 24 tons per 24 hours, variation in speed of rabbles.

TABLE 42.—RESULTS OF ROASTING AND LEACHING TESTS

Temperature		Roast			Extraction			
°C.	°F.	Time (hours)	Total S	S as SO ₄	Zn	Loss in weight	Zinc in tails	Extraction
593	1,100	7½	6.95	4.6	23.7	39.1	10.2	74.0
649	1,200	4	5.45	4.3	23.0	43.4	9.6	76.1
649	1,200	4½	6.3	5.4	23.0	38.0	9.2	75.1
704	1,300	4	5.35	4.35	23.0	36.0	10.8	70.6
704	1,300	4	4.8	4.4	22.8	29.0	10.3	68.0
760	1,400	3¾	4.75	4.35	23.6	32.6	12.5	64.4
815	1,500	4	5.05	4.31	23.8	27.4	11.5	65.0

¹ *Tr. Can. Min. Inst.*, 1917, XX, 174.

temperature are represented graphically in Fig. 200. They show that the percentage of extraction is highest at 1,200°F. or 650°C., and falls off quickly as the temperature is raised.

Working results of the Anaconda Copper Mining Co. at Great Falls, Mont., with Wedge roasters are shown in Figs. 201 and 202. A furnace is 25 ft. in diameter outside, 23 ft. inside, has seven roasting hearths and one open dryer hearth on top; the brick-lined shaft is 5 ft. in diameter, carries 26 water-cooled Kelly arms,¹ four for

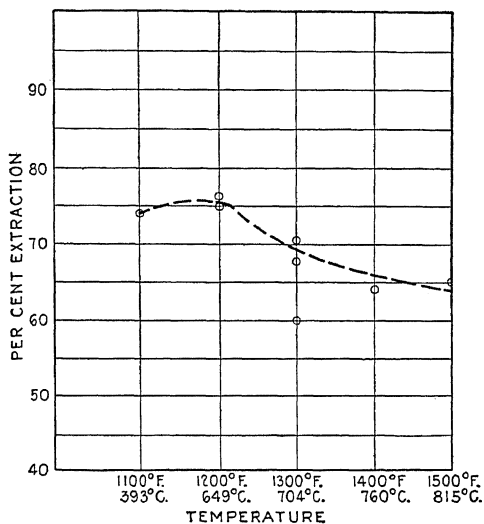


FIG. 200.—Sullivan concentrates; Wedge roaster, variation of temperature.

the dryer and the first hearth, and three for the other six hearths, and makes one revolution in 4 min.; the furnace carries two fire-boxes on each side of the seventh hearth in which fuel dust is burned; it treats from 40 to 45 tons concentrates in 24 hr.

Figure 201 represents the work with low-grade flotation concentrate which, on account of its fineness, undergoes great changes when dropping from one hearth to another. The elimination of S is more rapid at first than later owing to the oxidation of sulphides other than zinc; roasting of blende begins in earnest when the ore drops onto the third hearth which has a temperature of 640°C., after 25 per cent of the S has been eliminated; practically no sulphate is formed until the fourth hearth with 637°C., the highest

¹ Hofman, "Copper," 1918, p. 107.

temperature, is reached and 75 per cent of the S has been eliminated; from now on the formation of soluble sulphate is rapid and continues until the seventh hearth is reached; the roasted ore contains 5.3 per cent total S, and less than 0.5 per cent sulphide-S.

In Fig. 202, which represents the work with high-grade concentrate, the temperatures are higher than those noted in Fig. 201, as the oxidation of blende requires about 600°C. The second hearth

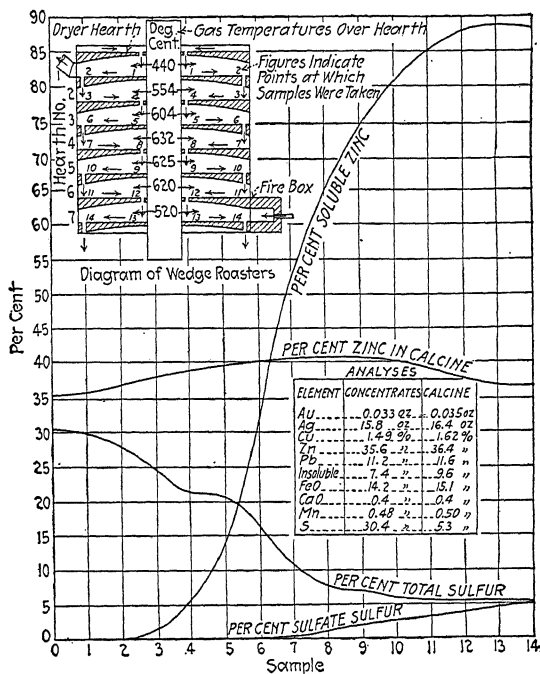


FIG. 201.—Roasting low-grade concentrates in Wedge furnace without returning flue dust.

has a temperature of 615° which rises to 700° on the sixth hearth, the elimination of S is more regular as it is due to the oxidation of blende; practically no sulphate is formed until the fifth hearth with 620°, when it increases slowly; the roasted ore contains 1.7 per cent total S, and only a trace of sulphide-S.

127. Lixiviation.—The leaching of zinc from the roasted ore with sulphuric acid is carried on in Pachuca tanks (see below), and usually in two stages which are termed *neutral leach* and *acid leach*.

In the neutral leach the solvent is made up of cell-acid (overflow

of end cells with 10 to 20 per cent H_2SO_4 and 2 to 3 per cent Zn) and of tailing solution of the acid leach (1 per cent H_2SO_4 plus 10 per cent Zn) in the proportion of about 20:80 in order to make a solvent with about 30 g. H_2SO_4 per liter; some MnO_2 is added to insure the complete peroxidation of iron, and perhaps some iron in the form of FeSO_4 in case there is not enough present to cover As

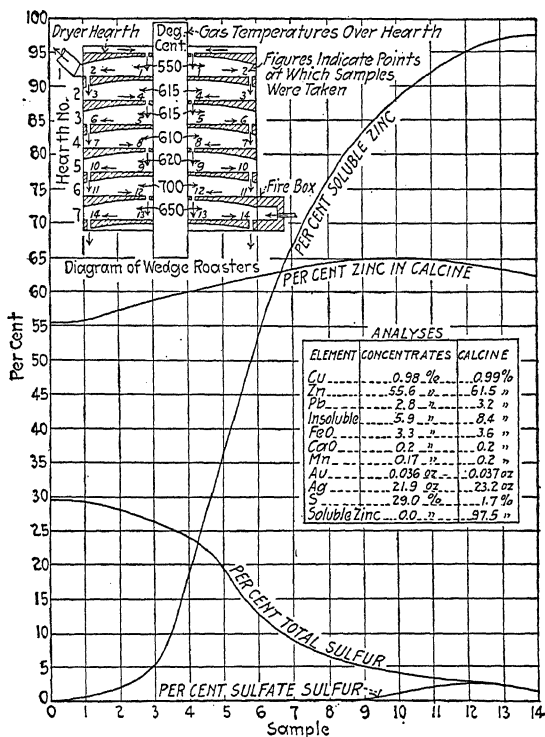
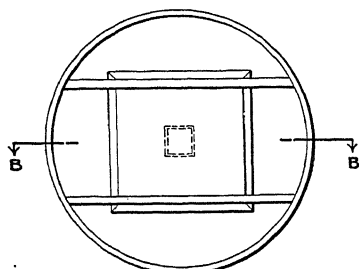


FIG. 202.—Roasting high-grade concentrates in Wedge furnace.

and Sb, also some pulverized limestone; roasted ore is the material to be treated. The whole is agitated in a series of Pachuca tanks (see below). The object of the operation is to dissolve part of the zinc (about 75 per cent) of the ore and to neutralize the free acid, to oxidize and precipitate the iron and with it all the arsenic and antimony, to precipitate a large part of the copper, and to coagulate gelatinous silica which becomes granular. The overflow from the Pachuca tanks passes into a drag classifier¹ to separate sand from

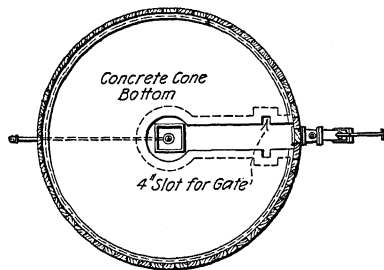
¹ Hofman, "General Metallurgy," 1913, p. 165.

slime. The sand may be ground and go to the acid leach, or may be first subjected to flotation to recover undecomposed blende, or may be smelted direct; the slime is conducted into a Dorr settler which gives a clear overflow and a spigot; the overflow goes to purification tanks, and the spigot to the acid leach.



Plan

FIG. 203



Section A-A

FIG. 205.

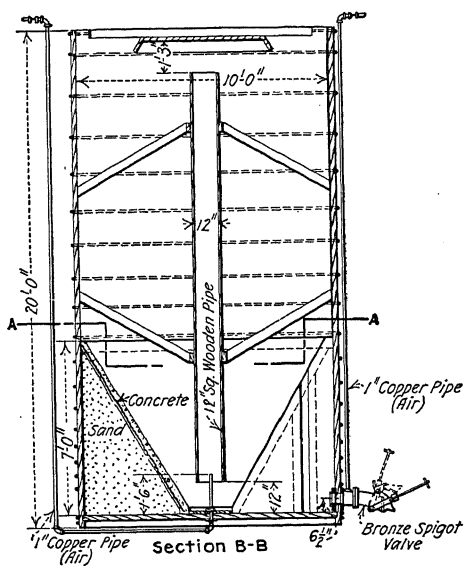


FIG. 204.

FIGS. 203, 204 and 205.—Pachuca tank.

In the acid leach the solvent is cell acid, about 80 per cent of the total. The material treated is a mixture of the ground sand and the spigot of the neutral settlers. The whole is agitated in Pachuca tanks until all extractable zinc (and copper) has been

dissolved and the free acid reduced to about $\frac{1}{2}$ per cent. The overflow runs to acid settlers which furnish a liquor that is used to make up the solvent on the neutral side, and a spigot which is filtered; the filter cake is usually smelted, the filtrate is added to the overflow of the acid settler. The overflow from the acid settler may first be freed from Cu and Cl by scrap Zn and Fe. It is essential that the free acid in the liquor from the acid leach be about $\frac{1}{2}$ per cent; an excess of acid causes an increase in the volume of solution which hinders settling, and augments the dissolved iron which has to be precipitated on the neutral side; a shortness of acid causes zinc to remain undissolved, and also an excessive moisture in the filter cakes on account of the presence of gelatinous iron salt, alumina, and silica.

The time it takes to leach a batch of ore is from 6 to 8 hr.

A sketch of a Pachuca or Brown tank is given in Figs. 203 to 205. It resembles the tank which has become a standard apparatus in cyaniding gold and silver ores;¹ it has been changed to meet the requirements of zinc lixiviation. The tank is a cylindrical wooden vessel into which is built a conical concrete bottom with a slope of about 60° ; the concrete rests on a sand foundation. In the center of the tank is a square wooden pipe (air lift) open at top and bottom, which is held in place by struts. At the bottom is a copper or lead pipe which delivers air under pressure, above the top is a plate which deflects the solution when it leaves the pipe. The cone has a gate for the discharge of the pulp, and the cylinder a port in the side closed by a spigot valve that serves the same purpose, compressed air from a 1-in. copper pipe assists the outflow. The compressed air causes the pulp in the pipe to rise; this overflows at the top and enters at the bottom thus keeping the particles in suspension and the pulp in circulation.

128. Purification.—The neutral solution from the neutral Dorr classifiers contains Cu, Cd, and traces of As and Sb, which have to be removed. The purification is carried on in Pachuca tanks by means of zinc dust or preferably atomized zinc. Copper is precipitated rapidly and cadmium slowly. This precipitation has to be carried on in a room that is well ventilated on account of the possibility of AsH_3 being evolved. Arsine² is a very poisonous gas, 0.5 mg. per liter has proved fatal to human beings. By drawing con-

¹ Hofman, "General Metallurgy," 1913, p. 717.

² Editor, *Chem. & Met.*, 1920, XXIII, 1, 243.

tinuously gas from the room through a silver nitrate solution traces of arsine are recognized by the formation of a dark precipitate.

In either case an excess of zinc is added at the end to ensure reduction of the Cd-content to 20 mg. per liter which is the limit if a first-class zinc is to be produced by electrolysis.

In operating, a tank is filled with solution, is agitated, and the necessary amount of zinc added gradually; the precipitation is finished in about 30 min., provided an excess of zinc has been used.

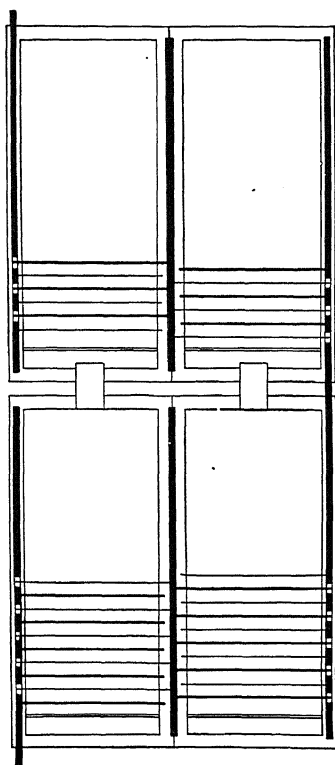


FIG. 206.—Arrangement of vats in pairs.

Fig. 206. The electrolyte is circulated by placing pairs of vats in cascades, one pair overflowing into the next, as indicated in Fig. 207; from the last pair the spent electrolyte, with about 10 to 12 per cent free acid and 2 to 3 per cent Zn, is collected in a sump and pumped to the storage tank of the leaching division. Special

¹ When this sludge is treated, there is real danger from arsine.

The tank contents are drawn into a classifier to recover the excess of zinc used followed by a Dorr settler, if copper was precipitated separately from cadmium; or if not, direct into a Dorr settler, which furnishes clarified solution and sludge; the solution is passed through a filter press to insure the clarity necessary for the cells, the sludge is stored as there is at present not sufficient demand for cadmium.¹

129. Electrolysis.—Little need be said from a general point of view in addition to that which was given in §124. Details are reserved for the discussion of the individual plants in §§132 to 134.

The multiple process is in use. In a cell, containing purified neutral electrolyte with about 60 gm. zinc per liter, x lead anodes and $x + 1$ aluminum cathodes, connected in multiple, are suspended from conductor bars. The cells, which are coupled in pairs are arranged in series as shown diagrammatically in

care is given to the proper ventilation of the building to carry off the fine spray of electrolyte which arises from the anodes by the liberation of oxygen gas; men have gas masks soaked with alkali for protection. On account of the large amount of spray, corrosion in a zinc plant is very noticeable, when compared with the familiar copper plant which works with soluble anodes. Every 48 hr. the zinc is stripped from the cathode to be melted into slabs; the aluminum cathode sheets are washed with hot water and roughened with a wire brush to ensure adhesion of the deposit. The anode deposit, MnO_2 and PbO_2 , is scraped and brushed off every 4 to 6 weeks; part of it goes back to the neutral leach.

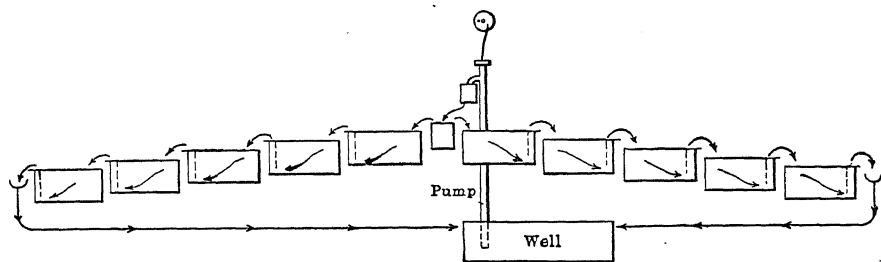


FIG. 207.—Circulation of electrolyte by disposition of vats in cascades.

130. Melting of Cathode.—The cathode sheets are melted in a coal-fired reverberatory furnace and cast. There is invariably formed 4 to 5 per cent dross, owing to the roughness of the cathode, caused by sheets being porous, one side being covered with sprouts, and to the presence of a coating of zinc sulphate. The dross contains as much as 40 to 50 per cent metallic zinc, which can be recovered in part by treating hot with ammonium chloride; the remaining dross is worked for oxides. In casting, the metal is dipped by means of long-handled ladles carried by overhead crawls, a ladle holds as much as 200 lb. zinc.

It is stated¹ that in 1919 a 1,000-kw. electric melting furnace of the carbon resistor type has been put in operation. The power consumption is said to be 70 to 80 kw.-hr. per ton metal and the metal loss in dross only 0.024 per cent. Experience at Great Falls is unfavorable to the electric furnace.

131. Treatment of Residue.—The working of the residue of the acid leach is governed by its character. If the ore treated was a lead-zinc ore, the residue is simply added to the bed of a lead blast

¹ Keeney, *Chem. Met. Eng.*, 1920, XXIII, 983.

furnace charge; if the ore was a copper-zinc ore, it is treated in a reverberatory furnace for matte, slag, and fume. Some plants have experimented with the Wetherill grate (§139), also with the Bartlett process;¹ the former yields 80 to 90 per cent of the Pb and 70 to 80 per cent of the Zn, but the cost is high; the latter gives a fair yield of Pb and Zn, but the tonnage is small.

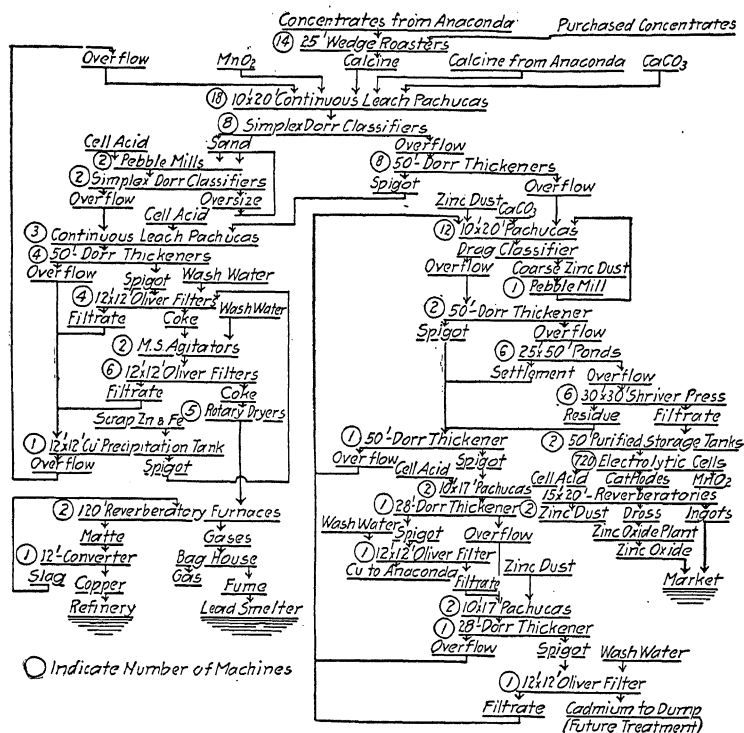


FIG. 208.—Flow sheet of 150-ton plant at Great Falls.

132. Anaconda Copper Mining Company, Great Falls, Mont.²

This plant since 1918 has a daily capacity of 150 tons spelter. The ore treated is a flotation concentrate containing some Cu, much Fe and Pb, and from 33 to 35 per cent Zn. Analyses of concentrate and calcine are given below, other data have been quoted in Figs. 201 and 202. The flowsheet is shown in Fig. 208.

¹ Hofman, "Lead," 1918, p. 135.

² Laist, Frick, Elton, and Caples, *Tr. A. I. M. E.*, 1920, LXIV, 699; Private Notes.

1. *Roasting*.—The ore is roasted in 14 Wedge furnaces. A roaster is 25 ft. in diameter outside and 23 ft. inside, has seven roasting hearths and one open dryer hearth on top; in the center is a 5-ft. brick-lined hollow revolving shaft which carries 26 water-cooled arms, four for the dryer, four for the first hearth, and three for the other six hearths; the speed of the arms can be varied, ordinarily they make 1 revolution in 4 min. The furnace has two fireboxes, one on each side of the seventh hearth, which are supplied with fuel dust under a pressure of 12 lb.; the fuel used is about 12 per cent of the weight of the ore. The furnace treats from 40 to 45 tons concentrate in 24 hr. The temperature of the furnace with low-grade ore is not allowed to exceed 625°C. on account of the danger of sintering, and gives with a concentrate of 31 per cent Zn a solubility of 85 per cent; with high-grade ore it reaches 700°C., *e.g.*, a concentrate with 55 per cent Zn gives a solubility of 95 per cent. The flue dust from the low-grade furnace goes back to the furnaces, that from the high grade is treated in the low grade, as it runs high in Fe and would cause the formation of ferrite if it were treated at the high temperatures desirable for rich ores. Table 43 gives analyses of low-grade concentrate and the calcine produced.

TABLE 43.—ANALYSES OF LOW-GRADE CONCENTRATE AND CALCINE

	Zn, per cent	Cu, per cent	Pb, per cent	Ag, oz.	Au, oz.	In- soluble, per cent	FeO, per cent	S, total	SO ₄ - S, per cent	Zn, soluble, per cent
Concentrate.....	30.5	1.8	9.5	16.5	0.06	6.5	20.0	34.5		
Calcine.....	33.0	1.9	10.3	17.8	0.07	7.4	22.3	4.5	3.7	82.7

It will be noted that the calcine contains undecomposed blende. If the roast were carried on to oxidize all the sulphide-S, there would be formed an increased amount of insoluble $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$; the blende can be recovered by the use of flotation apparatus in the lixiviation, the ferrite is permanently lost.

The plant treats also blende which has been roasted at Anaconda in 6-hearth 20-ft. McDougall copper roasting furnaces to which have been added fireplaces on the sixth hearth. A furnace treats 25 tons concentrate in 24 hr., reduces the S content from 35 to 4.5 per cent, and consumes 8 per cent coal. As the furnaces are not provided with drying hearths, the method of feeding flotation concentrates with 8 to 10 per cent water is of interest. The Lynn feeder is sketched in

Fig. 209.¹ The flotation concentrate is delivered from a hopper on to an apron feeder which discharges a panful at regular intervals on to a door revolving in a casing which incloses the receiving opening of the furnace. When the concentrate drops on to the floor, the impact of the ore sets spinning the door which discharges as quickly as it receives, and at the same time excludes the air. The shaft of the door is a $1\frac{1}{2}$ -in. gas pipe with six ribs welded to it and provided with a grease cup; to the ribs are bolted veins of $\frac{3}{8}$ -in. plate, 2 ft.

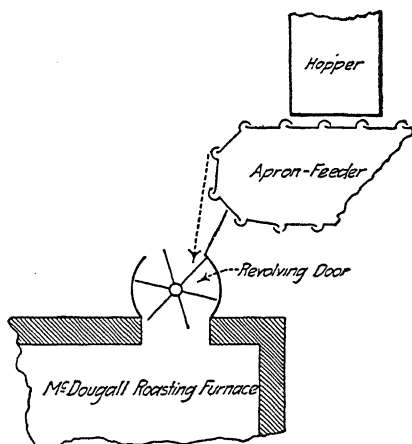


FIG. 209.—Lynn feeder of McDougall.

6 in. long and 9 in. wide; the shaft revolves on a $1\frac{3}{8}$ -in. iron rod which projects at the ends of the casing and is supported by bearings. The smaller McDougall furnace gives better results than the larger Wedge, *e.g.*, 85 vs. 82 per cent solubility. The difference is attributed to the fact that the Cottrell treaters, placed over the furnace, precipitate the SO_3 with the flue dust which is returned hot to the first hearth of the furnace when the treater plates are rapped. The SO_3 absorbs H_2O from the concentrate and is converted into H_2SO_4 which passes off as fume and has a decomposing effect on the dust. Experiments have shown that moistening of raw concentrate with H_2SO_4 before roasting increases the solubility of zinc.

2. *Lixiviation and Purification.*—A general plan of the leaching building is given in Fig. 210, and a cross-section through the division in Fig. 211. A view of one cascade is shown in Fig. 212. The flowsheet, Fig. 208 states that there are 24 Pachucas, 10 by

¹ *Min. Sci. Press*, 1919, CXIX, 58.

20 ft., which receive in 24 hr. 450 tons calcine, the necessary solvent, manganese dioxide, limerock, and return solutions from later stages in the process. As the process is continuous, the Pachucas are placed in series, seven tanks forming a unit.

For the first or *Neutral Leach*, the solvent is made up of cell acid (11.5 per cent H_2SO_4 , 2.5 per cent Zn) and partly spent liquor from the acid leach (0.6 per cent H_2SO_4 , 10 per cent Zn) to contain about 5 per cent H_2SO_4 . The solvent is prepared in tank 1 and the

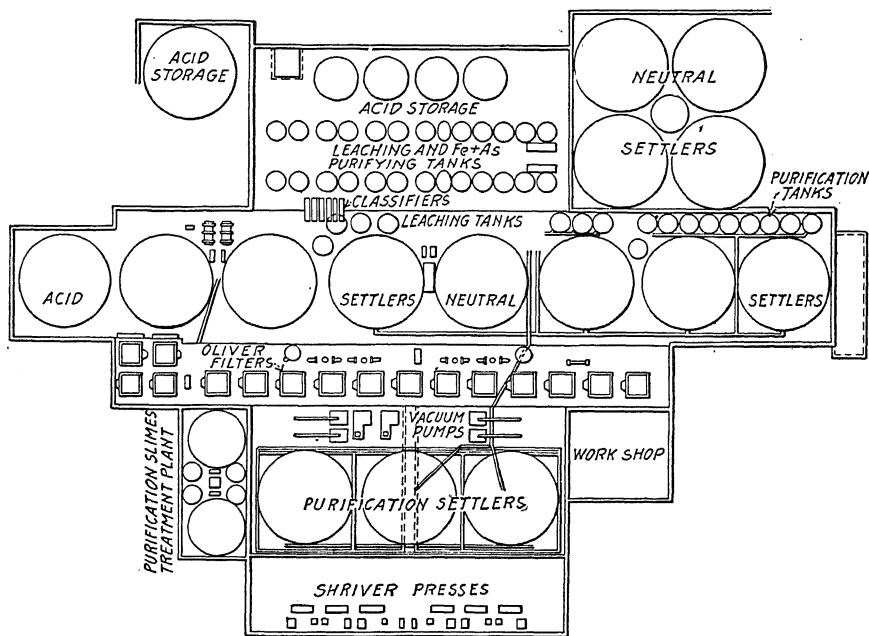


FIG. 210.—General plan of 150-ton leaching building at Great Falls.

necessary MnO_2 added. It overflows into tank 2. Ore is charged into tanks 2, 3, 4 to reduce the free acid in tank 4 to 0.5 per cent. Enough ore is added to tank 5 to neutralize the acid, and have a slight excess of ore. The neutral or slightly basic pulp current receives in tank 6 pulverized limestone and one-sixth of the total amount of calcine as excess base, to render granular gelatinous matter, to precipitate all the ferric iron and with it all the arsenic and antimony, and to throw down about 80 per cent of the copper. Tank 7 is a safety tank to give granulation and precipitation the time necessary to complete the reactions, and it is absolutely

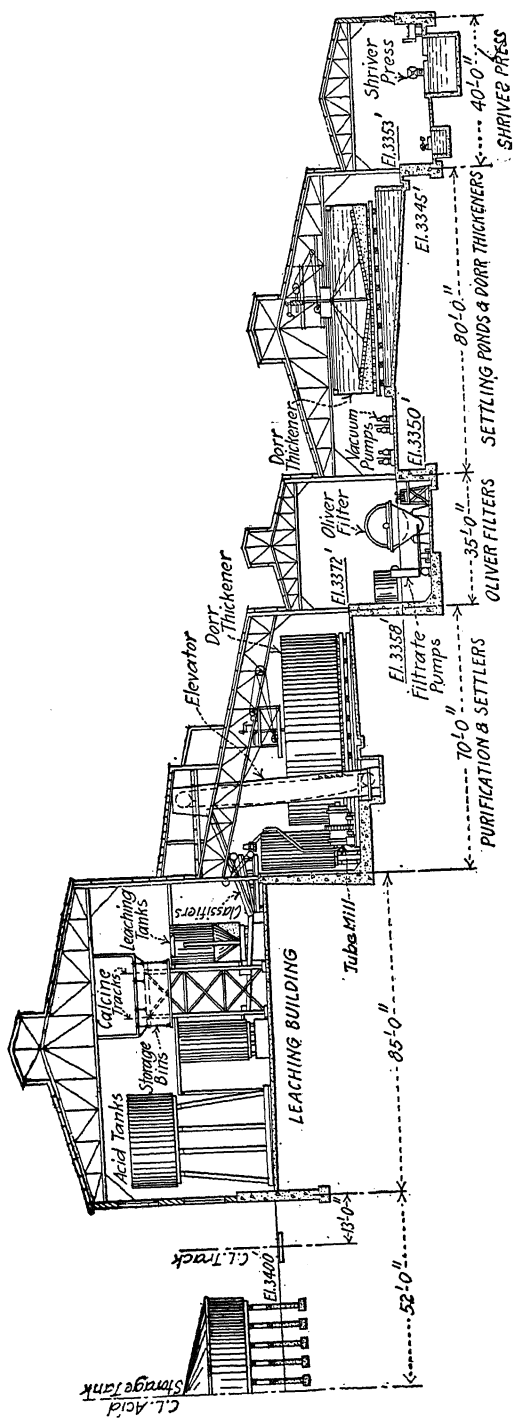


FIG. 211.—Cross-section through leaching division at Great Falls.

essential that this be the case. Tank 7 overflows into six Simplex Dorr classifiers (15 ft. long, 2 ft. wide, $1\frac{1}{2}$ ft. deep) which take out sands and furnish a pulp suited for settling.

The sands are ground with acid in two pebble mills (4 ft. 6 in. by 10 ft.) which are expected to furnish sandless pulp. For safety the product of a pebble mill is passed through a Simplex Dorr



FIG. 212.—Partly assembled cascade, showing anodes in place, insulator between cascade solution discharge pipe and return solution launder, also grating floor between cascades. Small track in foreground is for zinc cathode cars. Note overhead trolley arrangement.

classifier (15 ft. long, 2 ft. wide, $1\frac{1}{2}$ ft. deep); this gives a return sand to the pebble mills and overflow, which goes to the overflow of the Dorr thickeners of the acid leach.

The overflow from the neutral classifiers goes to eight 50-ft. Dorr thickeners which furnish clear overflow and spigot with 60 per cent solids.

This spigot and the spigot from the ground sand go to the *Acid Leach* in three 10- by 20-ft. continuous Pachucas in which cell acid (11.5 per cent H_2SO_4 , 2.5 per cent Zn) is the solvent; the additions

of ore and acid are so regulated that the overflow from the last tank is maintained at 0.5 per cent H_2SO_4 . The pulp goes to four 50-ft. Dorr thickeners which furnish overflow and spigot, the overflow goes to the first Pachucas while the spigot flows to four 12-by 12-ft. Oliver filters to be filtered and washed with hot water. The acid filtrate goes to the first Pachucas, the cake is pulped with hot water in Minerals Separation Co. agitators to assist in washing out zinc solution. The pulp is again filtered and washed in a second set of four 12-by 12-ft. Oliver filters. These furnish a filtrate to go to the first Pachucas and cake which is smelted as shown below.

The overflow from the eight 50-ft. Dorr thickeners and some return liquor are pumped into twelve 10-by 20-ft. Pachucas to which zinc dust is added (10 tons in 24 hours) to precipitate the Cu and Cd. The tanks are agitated for about 15 min. and discharged through a single drag classifier into two 10-by 50-ft. Dorr settlers in parallel, which deliver pulp to six settling concrete ponds, 25 by 65 ft., arranged in parallel, which are 7 ft. deep at the feed and 2.5 ft. at the discharge to facilitate cleaning. The settlement of the drag classifier is mostly excess zinc dust and is returned to the purification Pachucas after having been passed through a pebble mill. The overflow of the ponds goes to six 30-by 30-in. Shriver filter presses¹ which give clear electrolyte. The spigot from the two 50-ft. Dorr thickeners, the settlement of the ponds, and the cakes from the presses, all go to a single 50-ft. Dorr thickener, which furnishes overflow to be returned to the purification Pachucas and spigot. The spigot goes through two 10-by 17-ft. Pachucas until they are one-third full, then cell acid (10 per cent H_2SO_4) is added slowly, and agitation continued until a trace of copper goes into solution. The leaches are pumped into a 20-ft. Dorr thickener, which gives a spigot with about 30 per cent Cu; this is passed through a 12-by 12-ft. Oliver filter, and gives as cake a furnace product of copper and cadmium. The overflow from the thickener is treated with zinc dust (about 1 ton in 24 hr.) in two 10-by 17-ft. Pachucas to precipitate the cadmium. These deliver into a 28-ft. Dorr thickener which gives a spigot with about 12 per cent Cd for the Oliver filters and an overflow which is returned with the filtrate of the press to the purification Pachucas.

Figure 213 is a graphic representation of the chemistry of the neutral leach and the acid leach, and of the precipitation of copper and cadmium by means of zinc.

¹ Hofman, "General Metallurgy," 1913, pp. 720 and 724.

3. *Electrolysis*.—A cross-section of the tank room is given in Fig. 214, and a longitudinal section through a pair of cascades in Fig. 215; details of the tank are shown in Figs. 216 to 219. The tank house contains 864 cells which are divided into six electrical or solution units of 144 cells. The cells, arranged in pairs, form 12 double cascades which are separated from one another by aisles. The electrolyte coming through a 6-in. lead pipe is distributed to

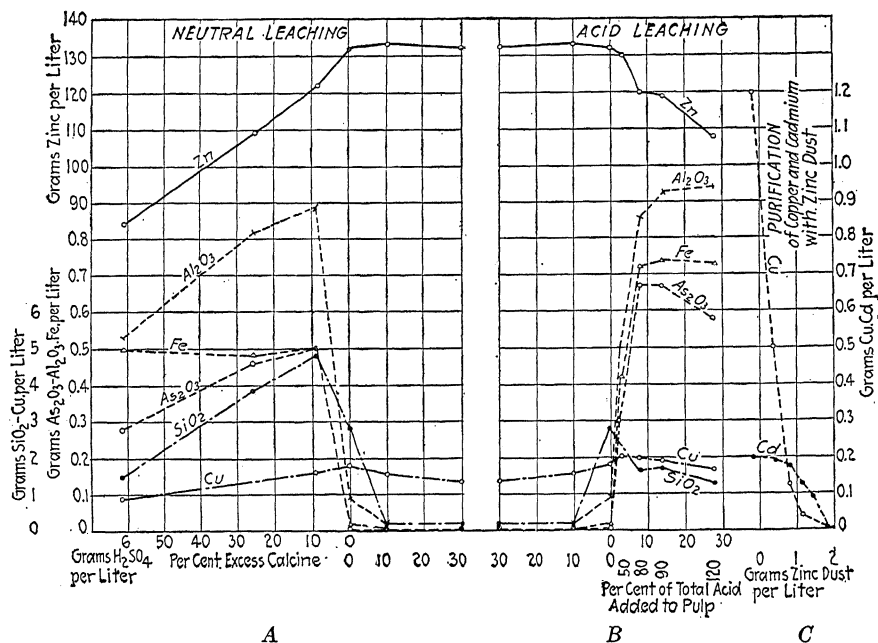
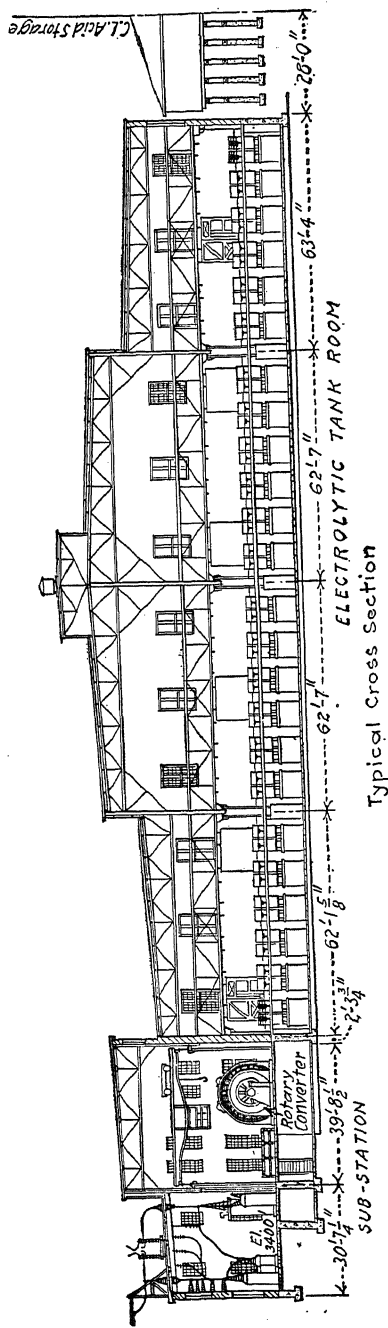
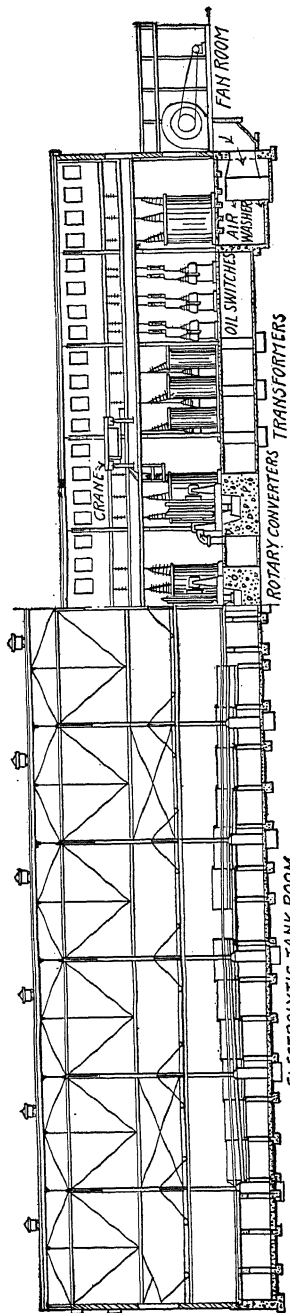


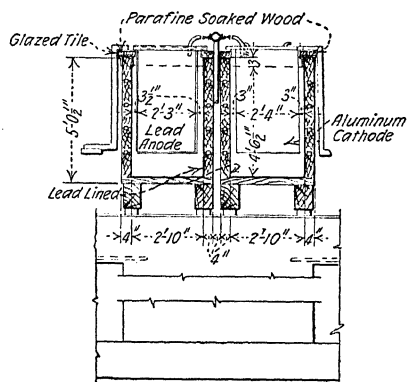
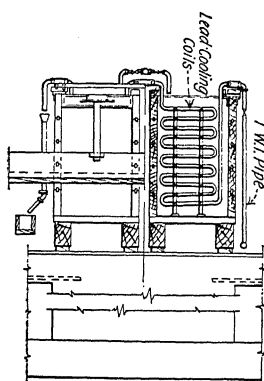
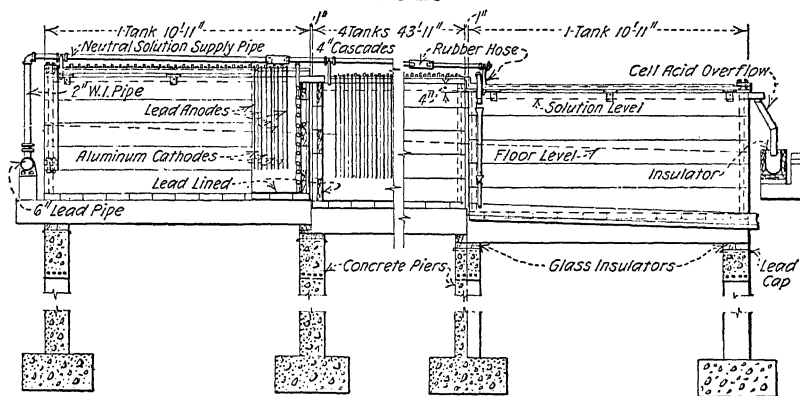
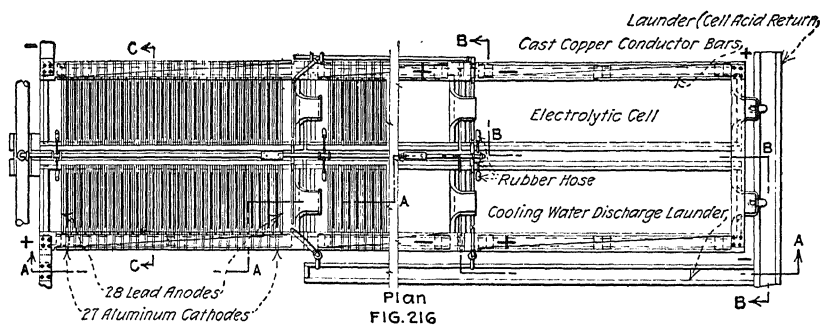
FIG. 213.—Graphic representation of the chemistry of (A) neutral leaching and precipitation of As_2O_3 , Fe , SiO_2 , Al_2O_3 ; (B) acid leaching of the thickened pulp from A; (C) zinc dust purification of the clear solution from A for Cu and Cd .

the cells through iron pipes with valves; it enters a top cell, flows from the sixth cell into a tail launder which carries the spent electrolyte to the acid storage tank. The 6-in. lines are broken and connected with 6 $\frac{5}{8}$ -in. rubber hose to prevent current ground. Electrolyte is fed into the first five pairs of cells of a cascade, the sixth pair is used as a control from which hourly samples are taken and tested for acid. The electrolyte flows at the rate of 800 liters per hour.

A cell is 10 ft. 3 in. long, 2 ft. 10 in. wide, and 5 ft. 0 in. deep; it is made of 4-in. plank, lined with lead, and tied at the ends with

FIG. 214.
Typical Cross SectionFIG. 215.
Typical Longitudinal Section
Showing One Pair of Cascades

FIGS. 214 AND 215.—Sections through pair of cascades.



FIGS. 216-219.—Tank details.

$\frac{3}{4}$ -in. iron bolts. It contains 28 lead anodes and 27 aluminum cathodes. A cathode is 2 ft. wide, 3 ft. 6 in. long, and $\frac{3}{16}$ in. thick; it is clamped between two copper crossbars, and is submerged for three feet; cathodes are spaced at 4-in. centers. On the sides they have wooden strips to prevent sprouting and to aid in stripping.

The anode is slightly smaller than the cathode; it is made of $\frac{3}{8}$ -in. chemical lead which is cast so as to completely inclose the cross-bar except a small place at one end where it rests on the conductor bar. Anodes are also spaced at 4-in. centers; this makes the electrode distance approximately $1\frac{3}{4}$ in.

Electrodes rest on Gillis conductor bars (U. S. Patent No. 1,276,208, Aug. 20, 1918), triangular copper bars with ribs which permit all the contacts to be on the side of the cell nearest the aisle, Fig. 216. This makes it unnecessary for the workman to lean over the tank in doing the work necessary at the contacts. Each tank has a cooling coil, Fig. 218, in order to maintain the temperature of the electrolyte at about 50°C.

The current supplied to 144 cells is 10,000 amp. at 520 to 580 volts, which gives a current density of 30 amp. per square foot. The drop across the cell when operating with 10 per cent acid and 10,000 amp. is 3.2 to 3.8 volts, depending on the temperature of the individual cell.

Cathodes are stripped every 48 hr., a sheet weighs from 15 to 20 lb.; the stripped cathode is washed with hot water and then surfaced with a wire brush when needed; nine cathodes are removed at one time for stripping by means of a frame attached to an overhead trolley and placed in a rack. Anodes are cleaned every 4 or 6 weeks. Zinc sheets are not washed before going to the melting division.

4. *Melting Cathodes.*—The cathodes are melted in two coal-fired reverberatory furnaces with a daily capacity of 75 to 90 tons; the hearth is 15 by 20 ft. and 2 ft. deep; the fireplace is 15 by 5 ft. and 3 ft. deep; the flue $2\frac{1}{2}$ by $2\frac{1}{2}$ ft. The hearth, built into an iron pan is made deep that it may hold a bath of metal and a big stock of cathodes; the roof has a charging opening; the fireplace is deep that it may be operated as a partial gas producer so that the gases will be reducing, and oxidation of metal avoided.

In melting cathodes there is formed about 5 per cent dross, as the sheets are porous, one side is covered by sprouts, and there is a coating of sulphate. The reverberatory is charged through the opening in the roof with 4 or 5 tons cathodes, these are lifted by an electric hoist and slid into the furnace by means of a roller coaster.

The melting metal running down a stack of cathodes carries with it dross which flows on top of the metal bath. At intervals the dross is rabbled with ammonium chloride which causes particles of entangled zinc to combine and sink into the bath. Once a day the furnace is cooled to 550°C . and the dross skimmed off the surface of the metal; it is worked hot with NH_4Cl in a modified cement mixer to which oil and sawdust are added to keep up the temperature. The metal set free collects at the bottom and is tapped into special molds. About 50 per cent of the metal in the dross is recovered. The total yield is 96.5 per cent spelter and 3.5 per cent zinc as dross, which assays 83.5 per cent Zn.

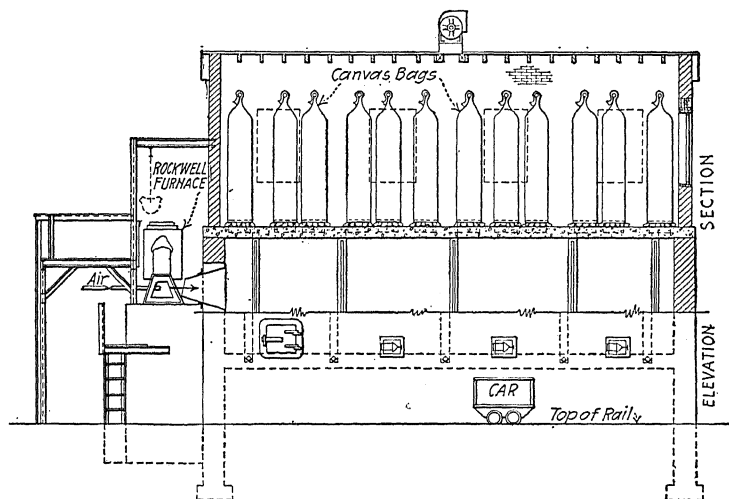


FIG. 220.—Zinc-dust plant.

The molten metal is dipped from forehearths with ladles holding over 200 lb. of zinc which are suspended from overhead crawls; it is poured into 50-lb. slab molds $15\frac{1}{2}$ by 10 by $1\frac{1}{2}$ in. There are 40 molds in line to a forehearth. A sample is taken from every twentieth ladle and cast into pencils in split graphite molds. The pencils of a day's production are broken up and combined to form the representative sample.

5. *Preparation of Zinc Dust.*—About 8 per cent of the zinc of the tank room is used in the form of zinc dust to precipitate copper and cadmium. There are two atomizing units, Fig. 220. Each consists of an oil-fired Rockwell furnace, size No. 3 with two blowing nozzles $\frac{3}{4}$ in. in diameter and a settling chamber, 10 by 30 ft., with

bags, 12 in. diameter by 10 ft. length, in the roof. The furnace is charged with molten zinc from the melting furnace by means of an electric hoist, ladle and crawl system; its carbon crucible has two holes $\frac{1}{8}$ in. in diameter; the flow of metal is regulated by two carbon rods so that the stream of metal is not over $\frac{3}{8}$ in. in diameter. The metal, which has to be hot, strikes the air which is under a pressure of 90 lb. The dust is drawn into cars from the chamber. A screen analysis of the dust showed on 20-mesh, 0.25 per cent; on 100-mesh, 16.09 per cent; through 200-mesh, 60.01 per cent.

6. *Treatment of Residue.*—The residue is smelted in reverberatory furnaces for matte which carries copper, lead and precious metal; for slag which carries zinc; and for fume which carries lead and is recovered after cooling in a baghouse. The matte is blown in a converter for blister copper, and escaping lead fume is recovered with that of the reverberatory furnace; the slag is put aside for the present, the extraction of zinc being postponed for a later date; the baghouse fume is sold to a lead smeltery.

The residue, averaging 15Pb , 13Zn , 2Cu , 29FeO , 12SiO_2 per cent and 25 oz. Ag and 0.07 oz. Au per ton, which comes from the Oliver filters is wet. It is dried in two 50-ft. Ruggles-Coles dryers and in three 9- by 70-ft. horizontal single-tube rotary dryers; the dryers are equipped with suction fans which deliver the gases to a double-compartment settling chamber and thence to the stack. The water content is reduced from 25 to 7 per cent.

The dried residue is conveyed to a concrete storage bin from which it is taken in 50-ton cars to the mixing plant. This consists of a large bin which has seven partitions to form eight 300-ton compartments, three for dried residue, one for fine coal, one for siliceous ore, one for copper concentrate, one for limestone, and one for return materials such as converter slag, cleanings, etc. The contents of the compartments are drawn in correct amounts on to a traveling conveyor belt which delivers into a bin, whence the mixed charge is drawn into 18-ton cars which discharge at short intervals into the charge hoppers of the two reverberatory furnaces.

The two reverberatory furnaces are 125 ft. long by 22 ft. wide, and 8 ft. high on the inside, the height at about the center of the furnace being the distance from the silica bottom to the arch of the roof; it is about 7 ft. at the flue and 9 ft. at the firing end. A furnace is coal dust fired by means of five burners, the charge is fed through ports in the roof, slag-skimming doors are placed on the end, and matte taps are placed on one side. The gases pass off through a

flue 10 ft. high and 8 ft. wide into four Sterling waste heat boilers arranged in parallel. The dust collecting in the flue and boilers is removed daily. From the boilers the gases travel to cooling pipes through a steel flue, 10 ft. in diameter and 1,200 ft. long, which has bottom discharge doors, these have the form of an inverted U; there are 30 pipes, each 30 in. in diameter and 130 ft. long, the pipes are provided with dampers. Should the gases not be cooled to 90°C., fresh air is drawn in between cooling pipes and fans. Draft is supplied by three fans, two are in use, one is held in reserve. Two fans have a capacity of 150,000 cu. ft. each per minute and are driven by 300-hp. motors; one has a capacity of 350,000 cu. ft. when operating against a combined draft and pressure of 6 in. water, the larger fan has a 600-hp. motor.

The gases from the pipes pass into a baghouse which has 17 sections, each with 138 collapsing bags 18 in. in diameter and 30 ft. long. Gas from the baghouse, which contains 0.5 per cent vol. SO_2 , is conducted through a wooden flue into the main-flue system. The dust collected in the hopper-shaped cellars of the sections is removed by screw conveyors to a cross conveyor which discharges into railroad cars for shipment.

In smelting, the slag aimed for contains SiO_2 27-28, FeO 29-30, CaO 16-17, ZnO 10 to 11 per cent. It is skimmed twice a shift into 15-ton slag pots and goes to the dump.

The matte is tapped into 15-ton ladles and blown in 12-ft. upright or Great Falls basic converters according to the method developed at Tooele,¹ i.e., it is first overblown without addition of silicious flux to expel as much lead as possible, then with the addition of fluxes to blister copper. The slag formed in blowing goes to the reverberatory furnaces; the fume to the baghouse collecting reverberatory fumes; the blister copper is cast into anodes to be refined electrolytically.

The yield in metal is Cu 90.78 per cent, Pb 72.65 per cent, Ag 93.04 per cent, Au 74.05 per cent.

133. Consolidated Mining & Smelting Co. of Canada,² Trail, B. C.—This plant, in operation since 1914, has a daily capacity of 75 tons of spelter. The ore treated comes from the Sullivan mine and contains about 6 per cent gangue, 5-20 Zn, and 5-15 per cent

¹ Hofman, "Lead," 1918, p. 419.

² Mason, *Min. Sci. Press*, 1920, CXX, 683.

Hamilton, *Tr. Am. Electrochem. Soc.*, 1917, XXXII, 321.

Chapman, *Chem. Met. Eng.*, 1920, XXIII, 227.

Pb. It is crushed very fine before it is subjected to flotation and magnetic concentrating processes. The concentrates contain 25–30 per cent Zn and 12–15 per cent Pb. An average analysis of the calcine shows Zn 27.0, Pb 11.1, Fe 25.8, Mn 0.09, CaO 1.8, Cu 0.03 per cent, and Ag 2.8 oz. per ton. The flowsheet is given in Fig. 221; in it *A* = acid leach, *N* = neutral leach, *P* = purification, *W* = washing.

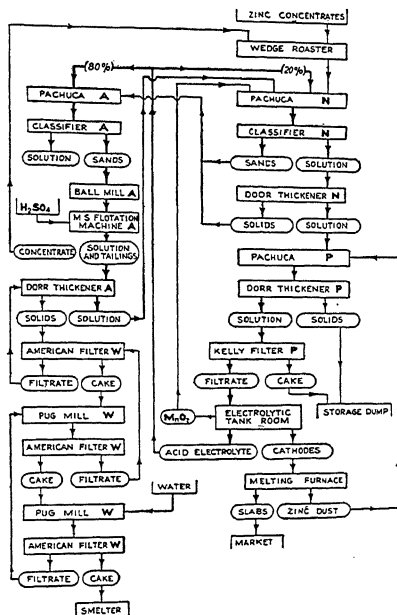


FIG. 221.—Flowsheet, Trail, B. C.

For the neutral leach there are two batteries of 10- by 30-ft. Pachuca agitating tanks, *N*, four to a battery, which treat the calcine with a solvent which is made up of the solution of the acid leach and 20 per cent of the acid solution from the electrolyzing tank which has been freed from most of its zinc. The necessary MnO_2 is added to the first tank of a battery. Zinc is dissolved and the solution neutralized, iron is oxidized and dissolved, it is precipitated in combination with arsenic and antimony, copper is thrown down in part, and colloids are coagulated. The overflow from the last tank of a battery runs into a pair of 15-ft. Dorr classifiers, *N*, in series, the sands from the first being re-treated in the second. The sands from the second classifier are pumped to the

1. *Roasting*.—The roasting is carried on in 13 Wedge furnaces, seven-hearth, 25 ft. in diameter, which are fired on the fifth or sixth hearth from two coal-fired combustion chambers placed at the opposite ends of a diameter of the furnace. The highest temperature reached is $700^{\circ}C.$; there is present in the calcine 3 per cent soluble $ZnSO_4$. A roaster treats in 24 hr. 40 tons dry ore.

2. *Lixiviation and Purification*.—There is a neutral leach and an acid leach; in fact the procedure is practically the same as at Great Falls, excepting that Great Falls has to

acid Pachucas, *A*. The overflow runs into a 40-ft. Dorr thickener, *N*. This thickener acts also as a distributor for four 40-ft. and three 32-ft. thickeners. The spigot from the eight tanks is pumped to the acid Pachucas, *A*; the overflow from the eight tanks is combined and delivered to three purifying Pachucas, 8 by 20 ft., in series, *P*. Zinc dust is added to the first tank to precipitate copper, cadmium, and the remaining traces of arsenic and antimony. The overflow from the third purifying tank goes to a Kelly filter press which gives filtrate going to two storage vats, 60 by 12 ft., in the tank room, while the cake and the spigot from the purifiers go together to a storage dump. The purified solution contains in grams per liter Zn 60, Fe 0.02, Cu 0.0005.

For the acid leach there are provided two batteries of 10- by 30-ft. Pachuca tanks, *A*, four to a battery. They receive the sands from the neutral classifier, *N*, and the spigot from the neutral Dorr classifiers, *N*. The solvent is the remaining 80 per cent of the acid solution from the electrolytic tanks which has been freed from most of its zinc. The overflow from the fourth tank of a battery goes into a pair of 15-ft. Dorr classifiers, *A*, which furnish solution to make up the solvent for the neutral leach in Pachucas, *N*, and sands. The sands from the second classifier are pulverized in a 6- by 6-ft. ball mill, *A*, the product of which is treated in two Minerals Separation Co. eight-cell flotation machines, *A*, with overflow from classifier, *A*. The machines furnish per day about 35 tons blende concentrate with 41 per cent Zn, which, after filtering in a 12- by 12-ft. Oliver filter go to one of the Wedge roasting furnaces, and a pulp, which with the filtrate of the Oliver filters, goes to seven 40-ft. thickeners, the flow to these being in parallel. The overflow from the thickeners, with its 0.2 per cent H_2SO_4 , goes to make up the solvent of the neutral Pachucas, *N*, while the spigot is passed through three American filters and two pug mills in series to remove completely the zinc solution. The American continuous filters (United Filter Corporation, 96 Broadway, New York) have eight 6-ft. disks. The cake from the last filter is dried and added to the lead blast furnace charge.

3. *Electrolysis*.—There are two tank rooms with 448 and 384 tanks, or 832 tanks in all. In tank room No. 2 with its 384 tanks the tanks are arranged, Fig. 222, in pairs; they form 24 parallel rows, eight tanks of a row forming a cascade with 4-in. fall, or 48 cascades in all. Tanks rest on concrete piers and are insulated from them by means of porcelain blocks. Between the rows are 30-in.

aisles, and at the end of the room is a floor space about 20 ft. wide for stripping cathodes which are loaded on to trucks and conveyed to the melting room. The tanks are made of cement concrete reinforced at the bottom and the corners by wire of chicken-wire mesh; a tank has a central longitudinal partition which divides it into two



FIG. 222.—Electric circuit in tank room.

cells, Fig. 223. The walls and bottom are 4 in. thick, the partition walls 6 in. The cells are lined with Trinidad asphalt $\frac{1}{4}$ in. in thickness, the outside of a tank is coated with asphalt paint. The cells are 27 in. wide, 82 in. long, and 36 in. deep. There is a 4-in. space between the ends of the tank; the overflow of electrolyte is through a 2-in. wood-fiber pipe. At the inlet of the tank is a wooden partition which extends to within 10 in. of the bottom and forces the

electrolyte to enter at the bottom, to travel diagonally through the tank, and to overflow through the wood-fiber pipe near the outlet at the opposite end. In the space between the tank wall and wooden partition is placed a coil of lead pipe, 30 ft. long and 1 in. in diameter for cooling-water; ten coils are provided for the eight cells, the two middle cells having two coils each, one placed at each end.

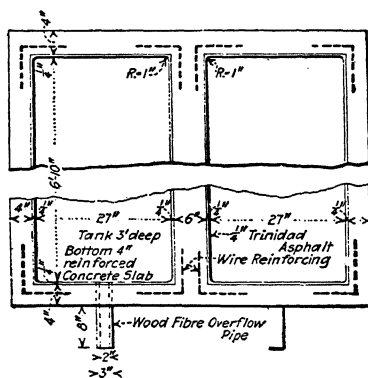


FIG. 223.—Plan of cell.

The neutral zinc solution runs from two storage tanks into an open launder from which it flows through iron pipes into the head-tanks of the cascade. The amount is regulated by a cock which is attached to the iron by short pieces of rubber hose. The circulating electrolyte is about 70 tons for 32 cells in 24 hr.; this makes the effluent from the eighth cell of a cascade to contain 20 to 25 g. Zn and 55 g. H_2SO_4 per liter.

There are 12 electric circuits, each circuit consisting of two rows of tanks, making 32 cells per circuit as shown in Fig. 222. Six motor-generator sets supply the current, each consists of one 1,158-kva., 2,200-volt, sixty-cycle, 600-r.p.m. induction motor direct connected to the 500-kw., 50/125-volt, 4,000-amp. direct-current generator. Each cell contains 17 anodes and 16 cathodes, which gives with 4,000 amp. a density of 24.2 amp. per square foot cathode area. The anodes are spaced at 4-in. centers, this gives an electrode distance of slightly less than 2 in.

The anode busbar is of cast lead, 5 in. high and 4 in. wide, Fig. 224; it rests on the outer wall of a tank and is insulated by porcelain

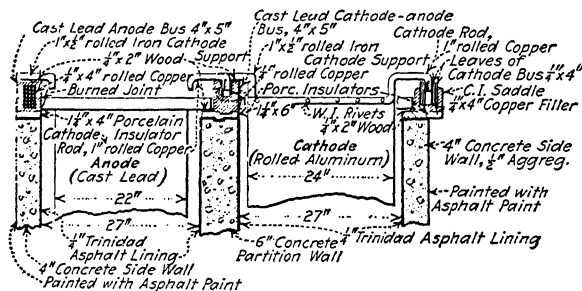


FIG. 224.—Busbars and electrodes.

blocks. Four strips of rolled copper, $\frac{1}{2}$ by 4 in., two extending to the full length and two one-half the length of the busbar, are cast into the lead. These extend beyond the lead, their free ends are clamped to filler strips of rolled copper, $\frac{1}{4}$ by 4 in., to make connection with the cathode bar of the next tank. The anode rods are burnt to the bar.

The anode-cathode busbar, on the partition wall of the two cells, is insulated by porcelain tiles. It is also of cast lead, 4 in. horizontal by 5 in. vertical; a slightly V-shaped slot, 1 in. wide by $2\frac{1}{2}$ in., faced with rolled copper plates extends the length of the bar. The tiles, 6 in. wide, have a groove, 2 by $\frac{3}{8}$ in., on the upper side, in which rests a tongue of the lead busbar; on the lower side a tongue is imbedded in the asphalt that covers the concrete of the partition wall. As the busbar is only 4 in. wide, a free space of 2 in. is left on one side upon which is placed a wooden strip 2 by $\frac{1}{4}$ in.; this acts as further insulator for the free ends of the anode rods, and as a support for them. The cathode rods are wedged into the slot, the anode rods are burnt on.

The cathode busbar is made of two strips of rolled copper, $\frac{1}{4}$ by 4 in., which are spaced 1 in. apart and extend the length of the tank. They are held in cast-iron saddles, and are insulated by porcelain plates, $9\frac{1}{2}$ by 6 by $1\frac{1}{4}$ in.; the saddles rest on flat porcelain insulators. Two additional strips of rolled copper, also $\frac{1}{4}$ by $4\frac{1}{4}$ in., one on each side of the center strips, extend one-half the length of the tank. The four strips are clamped to filler strips to make connection with the anode busbar of the next tank. The cathode rods are wedged into the 1-in. space.

The lead anode, Fig. 225, is 22 by 33 in. and $\frac{1}{4}$ in. thick; its upper end, 2 by $1\frac{1}{4}$ in., is cast around an iron rod, $\frac{1}{2}$ in. in diameter and

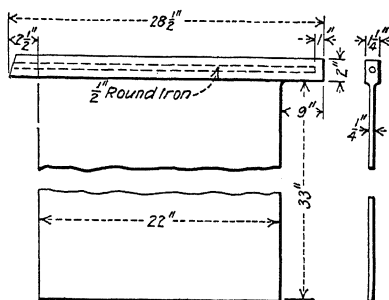


FIG. 225.—Anode.

$28\frac{1}{2}$ in. in length, which extends $2\frac{1}{2}$ in. on one side and 4 in. on the other side of the sheet. The shorter end is burnt to the cast-lead busbar, the longer end rests on a wooden insulator strip which in turn is carried by porcelain tiles covering the partition wall of the tank. The anode is immersed to a depth of 31 in.

The aluminum cathode, Fig. 226, is 24 by 36 in. and $\frac{1}{16}$ in. thick. Its rod is made up of two pieces, a copper rod, 1 in. in diameter, riveted for a distance of 16 in. to one side of the cathode, and a piece of strap iron, $\frac{1}{2}$ by 1 in., riveted for the same distance on the other. The copper rod, serving to make the electric connection, has at its end a slit to give it spring when it is wedged between the two copper plates of the anode-cathode busbar, or pushed into the space between the two copper plates, $\frac{1}{4}$ in. by 4 in., of the cathode bar. The cathodes have on the sides wooden strips, 25 in. long and 1 in. square with slits $\frac{1}{2}$ in. deep; they are to facilitate stripping of cathode zinc as, when removed, they expose the edge of the metal. The cathodes are removed one at a time by hand.

4. *Melting Cathodes.*—The 48-hr. stripped cathodes, weighing from 20 to 24 lb. are moved on trucks to the furnace building, where they are melted in a coal-fired reverberatory furnace having a capacity of 85 tons per day. The spelter is cast in iron molds by means of long-handled ladles carried by an overhead trolley. The dross formed is freed from adhering metal in a drum. Between $\frac{1}{2}$ and 1 per cent of the total zinc produced is atomized for the production of zinc dust for the precipitation of cadmium and copper.

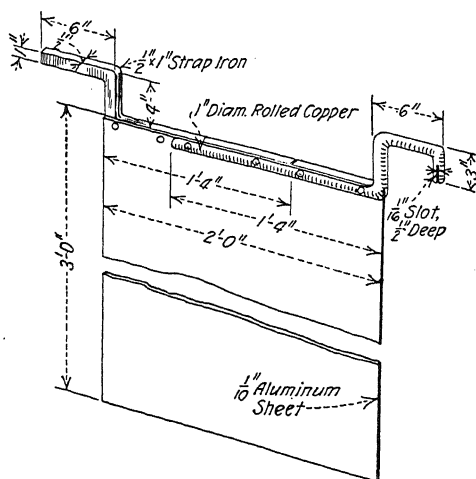


FIG. 226.—Cathode.

134. **Judge Mining & Smelting Co., Park City, Utah.**¹—This plant underwent numerous changes² before it developed its present practice. It treats daily 30 tons of concentrates and produces about 10 tons of spelter. The ore is a mixture of jig and table concentrates, ground in a Hardinge mill to 60-mesh, which contain 38 per cent Zn, 8 Fe, 5 SiO₂, 31 S, 3 $\frac{1}{2}$ per cent Pb and small amounts of Cu, Cd, Sb, As and Mn, and 0.15 oz. Ag per ton. The flowsheet is shown in Fig. 227.

1. *Roasting.*—The 60-mesh concentrate is roasted in a Wedge furnace, 25 ft. in diameter, which has seven hearths; it is fired on

¹ Austin, *Min. Sci. Press*, 1920, CXX, 409.

Chapman, *Chem. Met. Eng.*, 1920, XXII, 537.

Heikes, *Eng. Min. Jour.*, 1920, CX, 1,118.

Parsons, *Min. Sc. Press*, 1921, CXXII, 153.

² Hansen, *Met. Chem. Eng.*, 1917, XVII, 570.

the sixth hearth from two coal-fired fireboxes opposite to one another, the seventh hearth is devoted to cooling of the ore. The highest temperature is 700°C . The rabble arms on the second, third and sixth hearths, are water-cooled, the others are air-cooled. The hot calcine from the seventh hearth flows into a Baker cooler, a cylinder which revolves partly immersed in water.

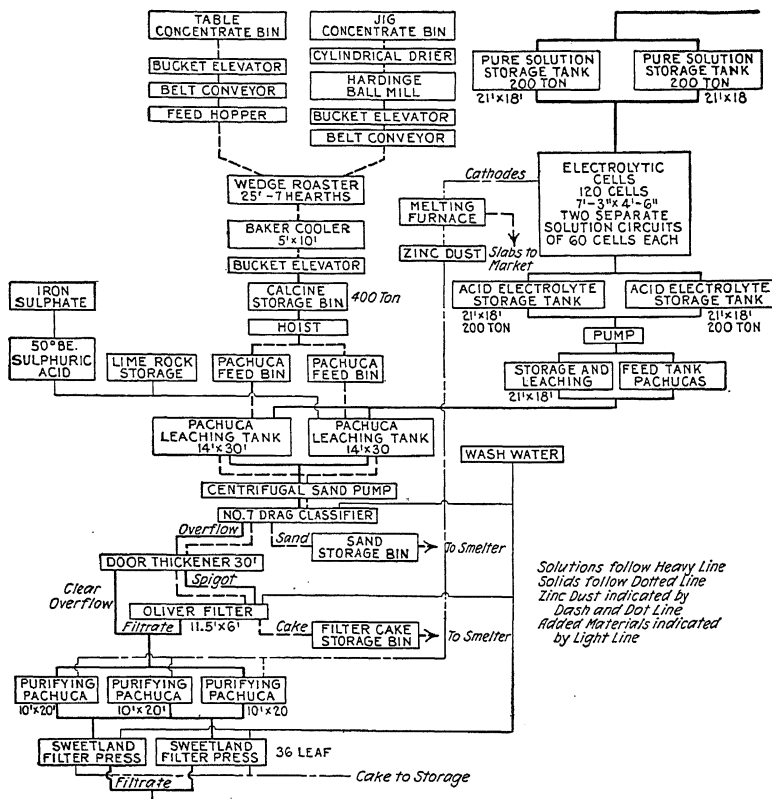


FIG. 227.—Flow sheet, Park City, Utah.

2. *Lixiviation and Purification.*—For this purpose there are provided two Pachuca tanks 14 by 30 ft., made of 3-in. redwood, which hold about 100 tons of solution. The solvent is acid electrolyte which has been freed from most of its zinc, reinforced by 70 lb. H_2SO_4 of 50°Bé. To the Pachucas is added FeSO_4 to make up for the lack of iron in the ore; it is intended that the solvent shall contain 0.3 g. Fe per liter. Limestone is added for the precipitation of

Fe in combination with As and Sb. The leach lasts from 8 to 10 hr. The sand from the drag classifier and the slime cake from the Oliver filter are not ground or washed as in the Great Falls and Trail plants, but go direct to the lead blast furnaces. This causes a loss in Zn and H_2SO_4 , and makes it necessary to add H_2SO_4 to the solvent. The sand carries 15 to 20 per cent Zn, the slime 10 to 12 per cent Zn, and together they contain about 12 per cent Pb and 28 Ag per ton.

The purification tanks are of 2-in. redwood; the agitation with zinc dust takes from 20 to 30 min. The purified solution is filtered in one of the two Sweetland filter presses; the press¹ has 36 leaves, each $3\frac{1}{2}$ ft. in diameter. The cake contains 40 to 50 per cent Zn, 4 to 7 per cent Cu, 3 to 6 per cent Cd. It is stored; a process for its treatment has been proposed. The purified solution contains in grams per liter Zn 60, Cd 0.004, Cu 0.003, Mn 0.4, Sb 0.001, As trace.

Electrodeposition.—There are 120 cells; 5 cells form a cascade with 3-in. fall; two cascades are placed side by side forming a bank of 10 cells; six banks form a section; the room has two sections. There are cross aisles between the banks, two aisles between the walls of the cell room and the sections, and one aisle between the two sections; the space is provided below the lower sections for stripping, etc.

Electrolyte from two storage tanks flows in two iron supply lines, through iron branch pipes supplied with valves, to the head tanks of the cascades; on leaving the lowest cells through iron pipes, the solution is collected in storage tanks and pumped to the leaching tanks.

Each section of 60 tanks is provided with a current of 5,000 amp. at 215 volts.

The tanks, of 2-in. redwood, are 7 ft. long, 3 ft. wide, and $4\frac{1}{2}$ ft. deep; the overflow chutes, 2 in. deep, are of chemical lead. A tank has an upright cooling coil at each end, which is a 1-in. lead pipe 40 ft. long and makes five 4-ft. loops.

Anode and cathode busbars are of rolled copper, Figs. 228 and 229. They are tapered from a cross-section $1\frac{1}{4}$ by 4 in. to $\frac{1}{2}$ in. at the free end; this saves copper, and is permissible, as the current carried decreases with each anode contact and increases with each cathode contact. Another way of accomplishing this is by means of the Gillis conductor bars in use at Great Falls (page 266). The bus-

¹ *Ill. Min. Sci. Press*, 1920, CXX, 411.

bars are placed on the side of the tank next to the aisle, and are supported by three wooden posts, 6 by 6 in., which are carried by separate concrete piers. The anode bars, placed on the inside, are $\frac{1}{4}$ in. lower than the cathode bar; the bars are insulated from each

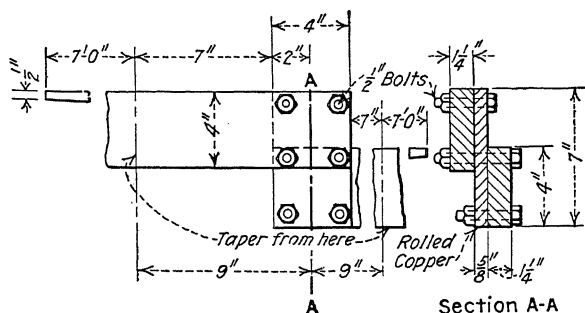


FIG. 228.—Details of busbar connection.

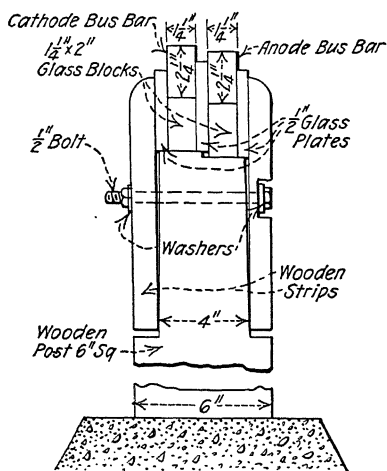


FIG. 229.—Details of busbar support.

other and from the wooden strips or guides by means of glass plates $\frac{1}{2}$ in. thick, and are supported by glass blocks $1\frac{1}{4}$ by 2 in. Connection between tanks is made by a plate of rolled copper $\frac{5}{8}$ by 4 in.; the plate is attached with $\frac{1}{2}$ -in. bolts to the inside cathode busbar and to the outside anode busbar.

The cast-lead anode is 21 in. wide, 38 in. long, and $\frac{1}{4}$ in. thick; the immersion depth is 33 in., Fig. 230. The supporting rod is a

rolled steel bar, 1 in. square; it extends 9 in. beyond the anode on one side where it is carried by a wooden strip, and 11 in. on the other where it rests on the anode busbar. Electric connection is made by a No. 00 copper wire which is burnt into the lead, passed through a hole in the steel bar and riveted on the under side.

The sheet-aluminum cathode is $\frac{1}{8}$ in. thick, its immersed area is 22 by 34 in. The wooden side strips are $\frac{3}{4}$ in. square and 36 in. long, they have a slot $\frac{1}{8}$ in. wide and $\frac{1}{4}$ in. deep.

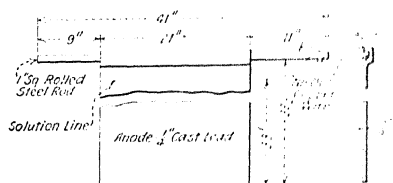


FIG. 230. —Lead anode.

A tank has 19 anodes and 18 cathodes, placed at 2-in. centers. A tank has 203.5 sq. ft. immersed cathode area and 174.25 anode area; with a current of 5,000 amp., this gives a current density of 24.5 amp. per square foot of cathode area. The voltage drop is 3.7 volts in the first cell and 3.3 volts in the last cell of a cascade; its average is $3\frac{1}{2}$ volts. The rate of flow of electrolyte is so regulated that the solution from the last cascade shall contain 60 g. H_2SO_4 per liter. A change in composition of electrolyte is shown in Table 44.

TABLE 44.—CHANGE IN COMPOSITION OF ELECTROLYTE

Item	Grams per liter					
	Zn	H_2SO_4	Cd	Cu	Sn	Mn
Feed at head cell....	59.5	0.2	0.003	0.0005	0.0005	0.0005
Overflow at tail cell..	21.7	58.1	tr.	0.0005	0.0005	0.0005

Cathodes are removed every 48 hr.; they are $\frac{1}{8}$ in. thick; they are taken out at one time by means of a frame of angle iron attached to a 1-ton chain-fall which runs on an overhead trolley. They are melted in a coal-fired reverberatory furnace, 5 by 8 ft. and 12 in. deep, having side charging doors, and cast into standard size slabs.

with ladles holding 50 lb. An average analysis of electrolytic spelter is Zn 99.930, Fe 0.005, Pb 0.038, Cd 0.027 per cent.

135. Other Plants.—The Bully Hill Copper Mining & Smelting Co.¹ ran for a while using rotating cathodes, but has stopped operations. In this connection the roasting of ores and the use of aerating anodes by Hanley is of interest.²

Electrolysis of sludge from acid chambers at Isabella, Tenn., is discussed by Broughton.³

136. Deposition from Chloride Solutions.—The leading process is that of Hoepfner⁴ which was in operation at Führfort, Germany, and is carried out in a modified form by Brunner, Mond & Co., at Winnington, Cheshire, England.

At Führfort the ore was burnt pyrite containing 10 to 12 per cent Zn mainly as ZnS; it was mixed with 18 to 22 per cent salt (95 per cent NaCl) and subjected to a chloridizing roast⁵ in muffle furnaces. The chloridized ore was leached, the solution concentrated to remove Na₂SO₄ by crystallization, then diluted and freed from Fe, Ni, Co, Cu, by additions of bleaching powder (Ca (OCl)₂ + CaCl₂) and pulverized limestone (CaCO₃), and from Pb, Cu, Cd, As, Tl, etc., by means of blue powder. The purified solution containing 0.08 to 0.12 per cent HCl was electrolyzed in V-shaped vats with a current of 9.2 amp. per square foot cathod earea at 3.3 to 3.8 volts. Stationary carbon anodes and rotating iron cathodes were separated by cloth diaphragms. The Cl set free at the anode was withdrawn and utilized in the manufacture of bleaching powder.

At Winnington the ore is given an oxidizing roast, and the ZnO formed converted into ZnCl₂ by means of CO₂ and CaCl₂, *viz.*, $\text{ZnO} + \text{CaCl}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{ZnCl}_2$. The solution is then purified as indicated above and electrolyzed. The Cl set free is utilized in the manufacture of bleaching powder; the spelter is 99.96 per cent pure.

¹ Hansen, *Met. Chem. Eng.*, 1916, XIV, 120.

² *Met. Chem. Eng.*, 1918, XVIII, 485.

³ *Chem. Met. Eng.*, 1919, XX, 392.

⁴ *Min. Ind.*, 1897, VI, 675; *Eng. Min. J.*, 1898, LXV, 252.

Günther, *op. cit.*, p. 99.

⁵ Stahl, *Berg. Hüttenm. Z.*, 1894, LIII, 1.

CHAPTER IX

MANUFACTURE OF ZINC OXIDE

137. General.—The zinc oxide found in the market may be classed as Pharmaceutical, French-process, and American-process Oxide.

Pharmaceutical Oxide.—This should not contain less than 99.5 per cent ZnO, the largest amount of lead permissible is 0.04 per cent PbSO₄. The oxide used to be prepared by precipitating ZnCO₃ from a purified solution of ZnSO₄, and calcining at a temperature between 300° and 400°C. Friedrich-Smith,¹ gives the dissociation temperature of smithsonite, ZnCO₃, at 395°C.

In recent years both the French and American processes have furnished the small amounts of pharmaceutical oxide needed; they are able to do this, as long as they start with raw materials that are free from harmful impurities, and do it at a lower cost.

French-process or Indirect-process.—This oxide, prepared by the vaporization of zinc and oxidation of the vapor by air and CO₂, is a very high-grade material which contains more lead than the pharmaceutical brand, but not more than 0.1 per cent PbO. The specification of the Bureau of Standards² calls for a fineness of 200-mesh, a minimum of 99 per cent ZnO, a maximum of 0.1 per cent total S, and one of 1 per cent impurity which includes moisture.

There are three grades in the market designated as White Seal, Green Seal, and Red Seal, which differ very little chemically, if at all. The highest grade, White Seal, is bulky on account of the fineness of the individual particles, and is of a brilliant white; Red Seal is less voluminous than white, and Green Seal less so than red. They are produced in one operation, but collected in different parts of the condensing system.

American or Direct-process Oxide.—This oxide is classed as lead-free and leaded.

Lead-free oxide, Horsehead Special, made from New Jersey oxide zinc ore by the New Jersey Zinc Co., is guaranteed to contain less than 0.1 per cent PbO. Analyses of the brand AZOZZZ made by the

¹ *Stahl u. Eisen*, 1911, XXXI, 1909; *Metallurgie*, 1912, IX, 409.

² Circular 88, Feb. 16, 1920.

American Zinc, Lead & Smelting Co. from Mascot ore, Tennessee, show the following range of composition: ZnO , 99.20–99.80; PbSO_4 , trace to 0.20; ZnSO_4 , 0.20–0.50; SO_2 trace to 0.02; moisture, trace to 0.10; total S, 0.04–0.15 per cent; sp. gr. 5.55. It is essential that ZnSO_4 shall not exceed 1 per cent, and SO_2 0.07 per cent. Specifications of the Bureau of Standards¹ say that the oxide should pass through a 200-mesh sieve, contain over 98 per cent ZnO , under 0.2 per cent total S, and less than 2 per cent impurity which includes moisture.

The standard brands of leaded oxides show PbSO_4 3 to 5, 8 to 12, and 35 to 37 per cent, depending upon the lead content of the charges treated. Specifications of the Bureau of Standards² distinguish between high-leaded and low-leaded oxide; both are to pass a 200-mesh screen; the high-leaded shall contain 60 per cent ZnO and over, the low-leaded 93 per cent and over; both shall contain 1 per cent and less water-soluble salts, and 1 per cent or less impurity including moisture. Leaded oxide forms a better paint than pure oxide; thus a mixture containing PbO amounting to a calculated 35 per cent PbSO_4 is considered to be the most satisfactory paint, both as regards body (the amount of oil it absorbs) and hiding power.

In addition to the three grades there are produced undetermined grades from the treatment of retort residues, and other intermediary products carrying lead and zinc. Thus *e.g.*, the old zinc-bearing lead and copper slags from the Lower Harz Mountains, Prussia, with 21 and 17 per cent Zn ³ are smelted by the Pape process: The slags are crushed, mixed with coke breeze, ground, briquetted with pitch, and the briquettes burned on a special grate. The hot gases carrying zinc and lead fumes are drawn by fans through brick dust chambers, waste-heat boilers, feed-water preheaters, iron cooling flues, diluted with false air, and forced through a baghouse.

Smelteries advertise their own special brands which they recommend for various purposes.

Lead-free oxide as a rule goes largely into rubber goods, especially automobile tires, enameled ware, porcelain, glass, oil cloth; leaded oxide goes mainly into paint manufacture.

Some of the leading books and papers dealing with zinc and lead paints are the following:

¹ Circular 88, Feb. 16, 1920.

² Circular 88, Feb. 16, 1920

³ *Glückauf*, 1910, XLVI, 237; *Eng. Min. J.*, 1920, LXXXIX, 819.

Breton "Relative Values of Zinc White and White Lead," *Compt. rend.*, 1903, CXXXVI, 1446; *Eng. Min. Jour.*, 1903, LXXVI, 201, 398.

Petit, G. and Grant, D., "The Manufacture and Comparative Merits of White Lead and Zinc White Paints," Scott, Greenwood & Co., London, 1907.

Holly, C. D., "The Lead and Zinc Pigments," Wiley, New York, 1909.

Wemple, L. E., "The Manufacture of Zinc Oxide for Pigment Purposes," Am. Zinc Institute, May 20, 1920.

138. French or Indirect Process.—The process is based on the volatilization of metallic zinc in retorts and the oxidation of the vapor by air or a mixture of air and of carbon dioxide. It was suggested by Le Claire, patented by Sorel, put into operation about 1844 at the works of the Vieille Montagne Co. at Valentin-Cocq, Belgium, and Mühlheim, Rhenish Prussia; about 30 years later, plants were erected in the Westphalian and Silesian zinc districts of Germany. The only plant in the United States is that of the New Jersey Zinc Co. at Florence, N. J.

The raw material used at the start by the Vieille Montagne Co. was a high-grade spelter practically free from lead, as lead being carried over by the zinc vapor would be oxidized and give the zinc oxide a tinge of yellow. At first cold air served to oxidize the zinc vapor. Later the air was heated by means of a coke fire; the hot air charged with CO_2 caused the entrained lead vapor to be oxidized to white carbonate. As a result, leady spelter was substituted for lead-free, even zinc drosses and galvanizer drosses have been used. The oxide is removed by a suction fan. In drawing oxide through dust chambers, air separation causes the heavier, denser, and inferior product to settle while the lighter, more voluminous and superior particles remain longer in suspension; the best grade is finally recovered in a filter chamber.

Zinc is volatilized in a single zinc smelting furnace holding one or oftener three or four rows of oval retorts with mouths pointing upward. A retort is 6 to 6.5 in. wide, 15 to 16 in. high, 43 to 44 in. long, and receives a charge of about 260 lb. spelter. It is either closed at one end or open at both ends. In the first case it rests on a ledge in the back wall; in the second it passes through the back wall and is closed by a tile luted in, the protruding lower end serves as charging and discharging opening. In either case the upper end passes through the front wall and terminates in the niche which serves as combustion chamber for the zinc fume. Air, heated by

passing through a low coke fire and thereby charged with CO_2 , is drawn into the niches and oxidizes the zinc fume; the oxide formed passes through hoods into a main, then through dust chambers, and is finally forced through a filtering chamber which has a volume of about 2,000 cu. ft. for the daily product of 1,000 lb. of a retort. A retort's charge is distilled and oxidized in 24 hr. with a fuel consumption of 800 lb. coal per net ton of oxide, and one-half day's labor. The cost in an eastern European plant producing 2,000 tons oxide a year is given by Lodin¹ per ton oxide in francs, which figured at 20 cts. is in dollars: fuel \$2.558, labor \$1.018, refractories \$0.494, steam and power \$0.500, maintenance \$1.322, diverse \$0.452, general \$2.482; total \$8.826; packing \$4.282; grand total \$13.108. He states that in western European plants the cost is larger on account of the higher price for fuel and labor; in the United States it is of course still larger.

The oxide plants in the Rhenish and Silesian provinces of Prussia use the single Rhenish furnace with three rows of large oval retorts for distillation, the furnace is gas-fired and provided with regenerators.

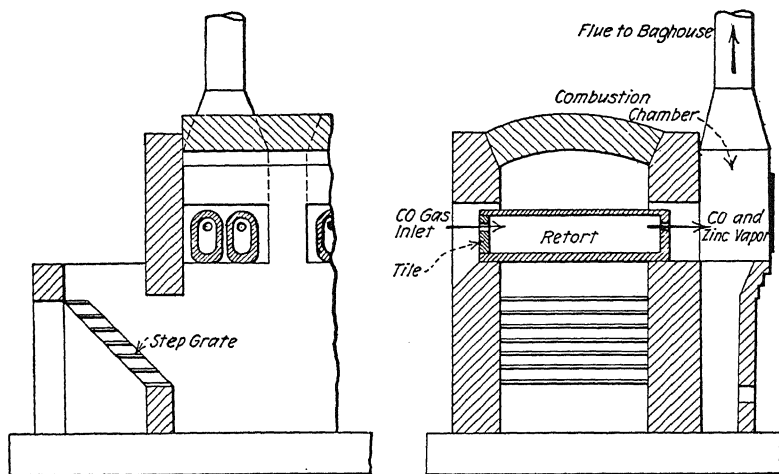
An oxide plant has recently been erected by the Broken Hill Associated Proprietary Smelters, Ltd., at Port Pirie, S. A.² It consists of a distilling furnace, a gas producer to furnish CO to the retorts, a retort baking oven, a baghouse, and a muffle furnace to heat the oxide. Vertical cross and longitudinal sections of the furnace are given in Figs. 231 and 232. The furnace, fired from a step grate, has a number of niches each with two oval retorts; at the front of a niche is an iron combustion chamber with flue ending in the cooling and settling main which carries the gases to the blower delivering into the baghouse. The open back or feed and discharge end of the retort is closed by a tile which has an opening for the admission of CO; the closed front end has a similar opening for the passage of zinc vapor and CO. The gas, which is to prevent oxidation in the retort and assist it outside, is prepared in a producer which is a shallow fireplace with grate on which coke is burned; from its closed top pipes conduct the gas into the retorts. The flame issuing from a newly charged retort has the bluish color of burning CO; as the temperature rises the flame turns pale green, then bright green as zinc vapor begins to come over and burn, and finally a brilliant yellow when zinc vapor comes over freely and

¹ "Metallurgie du Zinc," Dunod, Paris, 1905, p. 776.

² *Min. Mag.*, 1919, XXI, 58.

burns rapidly. The combined heat of the oxidation of zinc vapor and CO causes the flame to become a brilliant yellow white which is so intense that the attendant has to wear blue glasses. The fluffy oxide shaken from the bags contains much entangled air; it is therefore heated in a muffle furnace before it is packed.

Singmaster has patented (U. S. Patent, Nos. 1,372,462, March 22, 1921; *Chem. Met. Eng.*, 1921, XXIV, 895) a retort which operates continuously.



FIGS. 231 and 232.—Oxide furnace, Port Pirie, S. A.

139. American, Direct or Wetherill Process, General.¹—This process, invented by S. Wetherill in 1852, is based upon the reduction of ZnO by C, and the almost simultaneous oxidation of the Zn-vapor to ZnO by CO₂ and O; the oxide is drawn through settling chambers by a fan and then filtered in a baghouse, the residual clinker is worked up for its value.

¹ Williams, *Tr. A. I. M. E.*, 1876-77, V, 422.

Strecker, *Oest. Jahrb.*, 1879, XXVII, 282.

Clerc, *Min. Res. U. S.*, 1882, 374; also *Eng. Min. J.*, 1883 XXXVI, 148, 168, 180.

Ehrenwerth, Austrian Report on Mining and Metallurgy at Chicago Exposition of 1893, Vienna, 1895, p. 90.

Dürre, *Zt. Verein. deutsch. Ing.*, 1894, XXXVIII, 186.

Cregan, *Eng. Min. J.*, 1917, CIV, 675.

Stone, *Tr. A. I. M. E.*, 1917, LVII, 682.

Siebenthal, "The Zinc Pigment Industry," *Am. Zinc Inst.*, Chicago, May 10, 1920.

The process was carried out in 1852 at Newark, N. J., in 1853 at Bethlehem, Pa., and somewhat later at Bergen Point, N. J.; at present the plant of the New Jersey Zinc Co. at Palmerton, Pa., is the leading Eastern representative. As the oxide ore of Franklin Furnace used at South Bethlehem and Palmerton is practically free from lead, cadmium, and sulphur, the oxide produced is very pure. The process was taken up the latter part of the sixties in the Middle West and about 1880 in the Rocky Mountain district with oxide and roasted sulphide ores. As these are likely to contain lead, most of the plants produce leaded oxide. In 1919 there were in operation 18 plants; they produced 117,639 tons oxide valued at \$20,591,877. In recent years the zinc and part of the lead of retort residues are recovered in this manner.

A modification of the Wetherill process is that of F. L. Bartlett, which was started at Portland, Maine, in the eighties and transferred in 1896 to Canyon City, Colo. As the Bartlett process treats raw mixed sulphides and aims to produce a pigment of zinc oxide and lead sulphate, its details are passed over, especially as they have been given elsewhere.¹

140. Wetherill Process, East.—The characteristics of Eastern practice are that franklinite serves as ore and anthracite as fuel, that the working of the four or six furnaces in a block is separately controlled as regards blast and exhaust, that the oxidation of the zinc vapor is completed in the furnace in which the reduction of the oxide was affected, and that the oxide produced by the furnaces of a block passes through separate pipes into a main connected with dust chamber, fan, and baghouse. Two plants of the New Jersey Zinc Co., the former at South Bethlehem, Pa., and the present at Palmerton, Pa., may serve to discuss details.

*South Bethlehem, Pa.*²—The leading features of a block of six furnaces are given in Figs. 233 to 236; drawings of the plant have been published by Dürre, Ehrenwerth, and Strecker, and Dürre's drawings are found in the treatises of Ingalls, Lodin, and Liebig.

Figure 233 represents a vertical cross section, it shows two furnaces and part of a third of a block with vertical delivery pipes, horizontal main, brick cooling tower, suction fan, dust chamber and baghouse. Figure 234 is a longitudinal section of the furnace; Fig. 235 a cross

¹ Hofman, "Lead," 1918, p. 128-134.

² This plant was dismantled after the erection of the more modern plant at Palmerton, but some features of the older plant are of sufficient metallurgical importance to warrant their detailed description.

section of the two dust chambers; Fig. 236 a plan and part horizontal section of the baghouse.

The furnace, Figs. 233 and 234, is an oblong arched brick chamber, 10 by 4 ft. and 5 ft. high, divided by a Wetherill grate into two parts the laboratory and ash pit, 3 and 2 ft. high. The grate, adopted by Wetherill for his purpose, was in common use for boiler firing.¹ It consists of flat cast-iron plates, 6 ft. by 6 in. and 1 in.

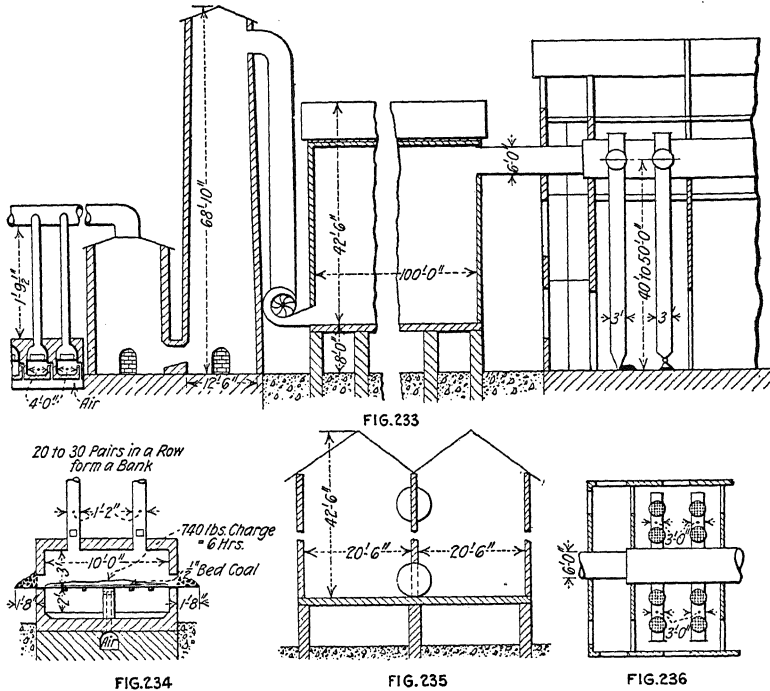


FIG. 234

FIG. 235

FIG. 236

FIGS. 233-236.—Oxide furnace, South Bethlehem, Pa.

thick, perforated by tapering holes, 1 in. at top $1\frac{1}{4}$ in. at bottom, about 100 to the square foot. The plates are placed closely together and supported by three or four transverse bars. The furnace is worked with undergrate blast. The air, delivered from a blower into an underground main, is withdrawn for each furnace by a branch pipe in the wall-division provided with a gate to regulate the volume and pressure, the latter is from 2 to 4 in. water. The ash pit, closed with a cast-iron hinged door, has a water sump for the protection of the grate. The arch has two openings for cast-

¹ Stone, *Tr. A. I. M. E.*, LVII, 682.

iron pipes, 14 in. in diameter, each provided with a hinged gate to permit regulation of air for the combustion of vapor and particles of coal; they deliver the dust- and fume-laden gases into a single boiler-iron flue. The front and back walls each has a semicircular opening above the grate for charging and discharging, which is closed by piling moistened ashes upon a cast iron shelf protruding about 20 in. The width of the opening is nearly the same as that of the grate. The two brick towers, Fig. 233, into which the overhead main delivers dust-laden gases serve to collect entrained ashes and other heavy particles. The first is wider and shorter than the second which has an inner diameter of 12 ft. 6 in. and a height of 68 ft. 10 in. Both towers have bricked-up doors for the removal of dust; a door has an opening which can be closed by a loose brick, it serves for inspection and for admission of air to burn any remaining zinc vapor and CO gas. The gases freed from coarse dust enter the suction fan and are driven through the cooling chamber. Two such chambers, used alternately, are shown in Fig. 235. A chamber, 100 ft. long, 20 ft. wide, and 42 ft. 6 in. high, forms a frame building plastered on the inside and provided with a roof of corrugated iron. About 10 ft. from the bottom it is provided with a V-shaped sheet-iron bottom which extends the length of the building and is supported by brick piers; it collects fine dust and impure oxide which are discharged through pipes extending through the floor. The collected material is moist and has to be dried before it is added to the ore charges of the zinc smelting furnaces. The cooled and dust-free gas enters the baghouse through a horizontal distributing pipe placed beneath the roof; this has branches from which are suspended cotton bags 30 to 40 ft. long and 3 ft. in diameter. The bottom of a bag is tied with a cord or simply twisted for the collection of oxide. A bag is shaken morning and evening to detach the oxide from the side and free the pores of the cloth. There are provided 200 sq. ft. of bag surface for 1 sq. ft. grate area. The oxide is removed once or twice a day, dried if necessary to expel moisture, screened to remove fibers or other foreign particles, and packed in barrels. Details are taken up with the Palmerton plant.

The ore used is a franklinite concentrate. The product of the mine is crushed and washed to remove the gangue, and then franklinite separated from willemite and zincite by magnetic concentration. Of the mine analyses by Stone¹ four, shown in Table 45, give the compositions of four grades of ore.

¹ *Eng. Min. J.*, 1886, XLI, 208.

TABLE 45.—COMPOSITION OF ORE AT SOUTH BETHLEHEM, PA.

SiO ₂	11.08	10.28	4.43	9.78
Fe ₂ O ₃	27.54	30.46	30.13	27.20
MnO.....	17.63	15.66	12.21	17.81
ZnO.....	35.88	27.15	27.12	22.94
CaO.....	2.01	8.45	12.63	11.46
MgO.....	0.77	0.91	1.69	0.74
Al ₂ O ₃	0.24	0.09		0.67
Fe.....	19.28	21.32	21.09	19.04
Mn.....	13.65	12.12	9.46	13.79
Zn.....	28.78	21.79	21.76	18.41

Other analyses have been published by Ricketts.¹ The franklinite concentrate averages 22 per cent Zn.

Management.—Supposing a charge to have been worked off, the furnace-man removes the ashes closing the working doors, breaks up and removes the residuum, a more or less clinkered mass which covers the grate; he spreads over the grate a layer of anthracite, buckwheat No. 2, to a thickness of $\frac{1}{2}$ in., that is from 150 to 200 lb., closes the door with a piece of sheet iron and lets on a little blast, the fuel having been brought to the ignition point by the heat radiated from the roof and the sides of the furnace; he spreads a slightly moistened charge of 740 lb. consisting of equal parts of ore and anthracite to a thickness of 4 or 5 in., not exceeding 6 in., closes the working door with ashes put aside when the preceding charge was to be drawn, and turns on full blast.

The C burns to CO₂, in part to CO; it acts upon zinc oxide, $C + 2ZnO \rightleftharpoons Zn_2 + CO_2$ or $C + ZnO = Zn + CO$; the zinc vapor is oxidized, $Zn + CO_2 \rightleftharpoons ZnO + CO$, $Zn + O = ZnO$; the carbon monoxide is burnt, $CO + O = CO_2$.

A charge remains in the furnace 6 hr., when 83 per cent of the Zn will have been converted into ZnO. One man has charge of six furnaces, he therefore charges and discharges one furnace every hour; he watches the admission of air, sees that the blast passes uniformly through the charge and that no blow-holes are formed.

The residuum forms about 66 per cent of the weight of the charge, and averages Zn 6, Fe 40, Mn 11, SiO₂ 20, P 0.026.² It is smelted for spiegeleisen with 10 to 20 per cent manganese; 100 tons residuum give 50 tons of spiegeleisen and 4 tons of impure oxide. Dust and impure oxide go to the oxide or spelter furnaces. The oxide

¹ *Eng. Min. J.*, 1883, XXXV, 235.

² Analyses by Stone, *Eng. Min. J.*, 1886, XLI, 208.

of first grade contains 99.87 per cent ZnO, that of second grade 99.34 per cent ZnO.

Palmerton, Pa.—The works, begun in 1900, have taken the place of the older plant at South Bethlehem; the main features of the latter have been retained, but details have been changed and represent the latest word as regards Eastern Practice. There are two divisions, the old Western plant with 34 blocks of furnaces, and the more recent Eastern plant with 26 blocks. The Eastern plant is shown in plan and three vertical sections in Figs. 237 to

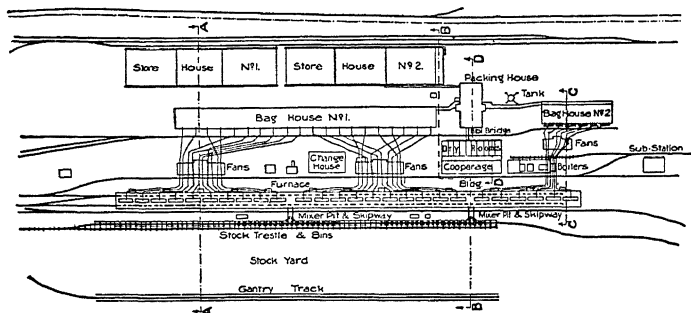
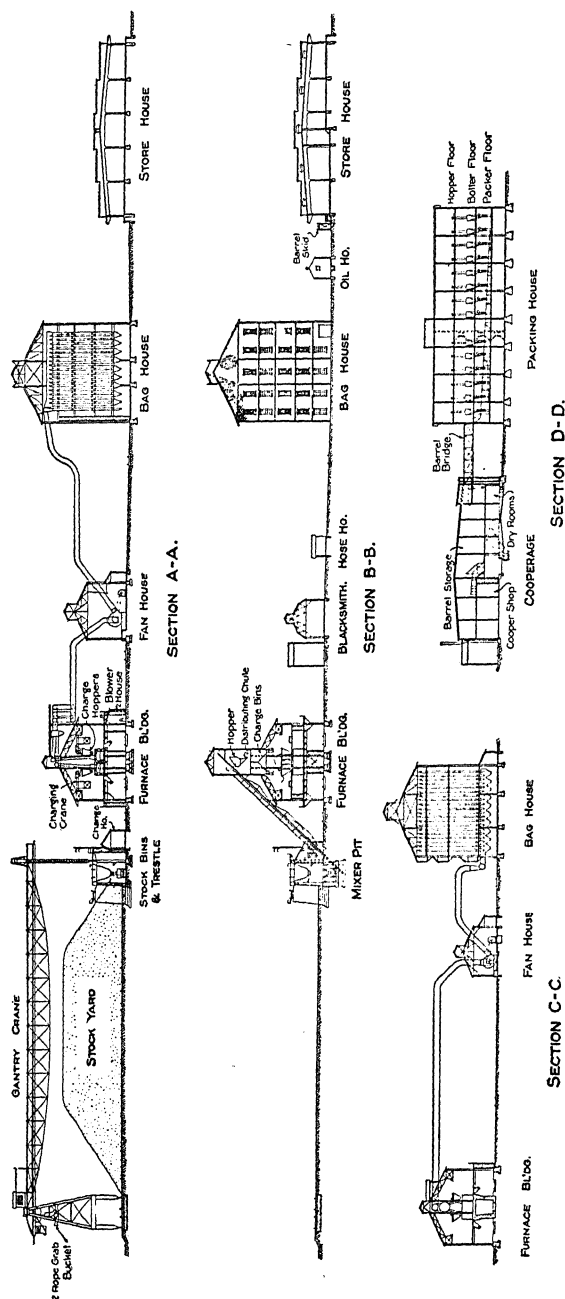


FIG. 237.—Plan of East Plant, Palmerton.

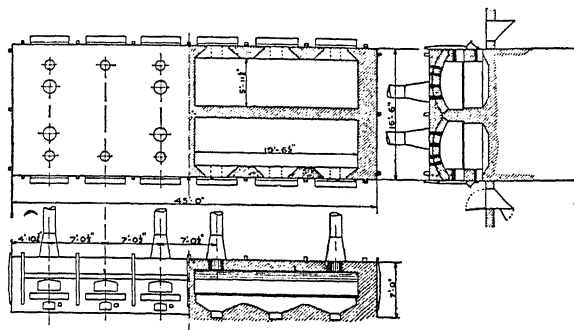
240. On the south side is the stockyard to receive ore and fuel. As the ore represents raw and roasted concentrate of about $\frac{3}{8}$ in., and the coal is washed anthracite, buckwheat No. 2, $\frac{3}{16}$ to $\frac{3}{8}$ in. in size, no provision is made for crushing. Fluxes that may be necessary, are crushed to $\frac{3}{8}$ in. size in another part of the plant. The ore and coal arrive on the double-track trestle, 22 ft. high, and are delivered into Brown tangential bins next to the furnace building. Material to be stocked is removed from the bins to the stockyard by means of a gantry crane of 233 ft. 9 in. span with two 10-ton Brown grab buckets; the same equipment transfers materials from the stock-pile to the bins. In making up charges, the materials are drawn from the bins into a weighing larry which has two hoppers, each capable of holding a furnace charge. The contents of a larry are discharged into Ransome concrete mixers, Fig. 84, placed in the mixer pits, and the mixed charges elevated by inclined counter-balanced skips to the bins above the furnaces. From the bins the mixture is conveyed to the furnaces by cranes, each of which has three hoppers holding one-third of a furnace charge. The hoppers are placed on a scale to regulate the equal distribution of the charge.



FIGS. 238, 239 and 240.—Sections of East Plant, Palmerton, Pa.

The correct amounts of charge are held in hoppers over the furnaces; in this manner the time required between drawing the clinker and starting the blast for a new charge is reduced to 35 min. In the furnace room the blocks of furnaces are sufficiently elevated to permit dropping the clinkers into hoppers below the working floor and thence into cars.

Each block has its own blast and flue connections. The blast is derived from two blowers in a separate small building and distributed to the blocks. The suction for each block is furnished by an 8-ft. fan made of heavy plate, it has Hyatt roller bearings and a water-cooled shaft. The fans are assembled in three buildings.



FIGS. 241, 242 and 243.—Oxide furnace, Palmerton, Pa.

The pipes leading from the burners to the baghouse are 3 ft. in diameter and of No. 16 sheet iron; they have clean-out openings and ports to draw in false air for the cooling of the gases which travel at a speed of 40 ft. a second. The gases are filtered in two baghouses, a large and a small one; larger rooms are more economical in labor and offer no inconvenience provided they are well ventilated. The bags, 22 in. in diameter and about 40 ft. long, are made of closely woven cotton. In the majority of cases the gases enter a header at the top of the room, pass from this into a series of horizontal branch pipes, and descend in bags tied to the bottom nipples of the pipes. Four bags are tied to the top nipples of a sheet-iron hopper having the form of an inverted pyramid; the smaller bottom end is attached to a single collecting bag. When the bags are to be shaken, two branch pipes connecting with a single line of collecting bags are cut off at a time. The filtering surface necessary in relation to the grate area formerly was deemed to be 130:1; it has been reduced to 80:1. Of course, such a ratio holds good only for an ore

mixture producing a given amount of oxide; with a mixture richer in zinc, the filtering area would have to be correspondingly larger. The automatic baghouse of Brooks & Duncan which greatly reduces the filtering surface necessary is taken up in §105. With some furnaces, the gases enter the bottoms of the bags. It has been found that the oxide collected contains less H_2O and SO_2 than that obtained from gases entering at the top.

The furnaces of both divisions are alike. A furnace block with four hearths is shown in plan, elevation and sections in Figs. 241 to 243. The block is 45 ft. long and 16 ft. 6 in. wide. A hearth is 19 ft. $6\frac{1}{2}$ in. by 5 ft. $11\frac{1}{2}$ in., has in the roof three charge openings surrounded by hoppers, two pipes, 20 to 22 in. in diameter, for the withdrawal of gases; on the side are three working openings closed by doors. It treats 3 charges in 24 hr.; a charge is therefore worked in 8 hr. The hearths are charged at 2-hr. intervals in regular order, so that in the 8-hr. period one furnace is starting, one finishing, and two are working strongly. The result is that the volume and temperature of gases are approximately uniform. The gases from the 8 pipes pass into a drum-pipe overhead which has an outlet in the center leading to the exhaust fan.

Supposing the charge of a hearth has been worked off, the hearth is cut off from the bagroom by closing the dampers in the flue, the blast is shut off, and the working doors are taken down. Three men serve 24 doors in 8 hr. The three men working together rake off the loose material on top of the charge and drop it in heaps on the floor. They break up the clinker with heavy slice bars, rake it into hoppers under the floor and free the side and back walls from adhering clinker. Now they drop 250 lb. or 9 per cent bed coal per door, close the doors and admit a light blast for about 5 min. When the bed coal burns evenly and brightly, an ore charge of 2,700 lb. (900 lb. No. 2 or 3 buckwheat anthracite and 1,800 lb. franklinite) is dropped through each of the three charge hoppers and leveled to a thickness of 8 in.; the doors are closed and the blast is turned on to a pressure 0.2 in. water; later when clinkers form the pressure rises to 3 in. The work on the hearth is finished, the hearth is left to itself, inspected on and off to stop any blowholes. The gases pass off into the open by a side pass until after about $1\frac{1}{2}$ hr. zinc vapors appear. The side pass is closed and the damper leading to the oxide flue opened.

The ore used is of three different grades. Franklinite, Zn 18.2, Fe 35.0, Mn 12.8, SiO_2 3.6, which is worked alone and the residue

smelted for spiegeleisen—half and half, Zn, 18.4, Fe 15.2, Mn 12.2, SiO_2 12.6 and Dust, Zn 70.6, Fe 20.1, Mn 8.9, SiO_2 7.2 which are worked together, the residue goes to waste, as it contains too little Fe and Mn, and too much SiO_2 to make smelting profitable. For a

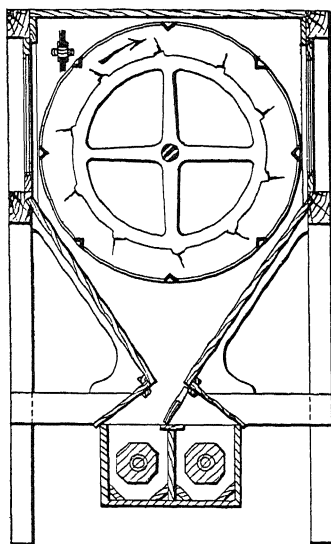


FIG. 244 END SECTION OF MACHINE WITH TWO CONVEYORS

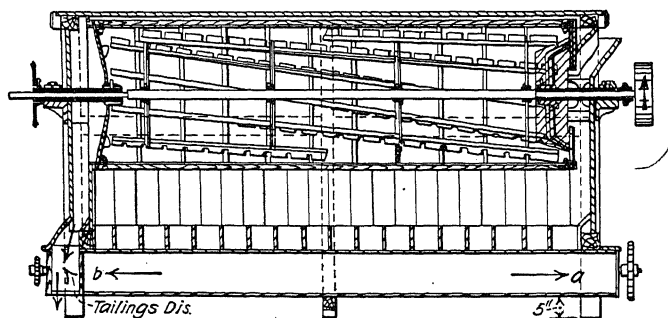


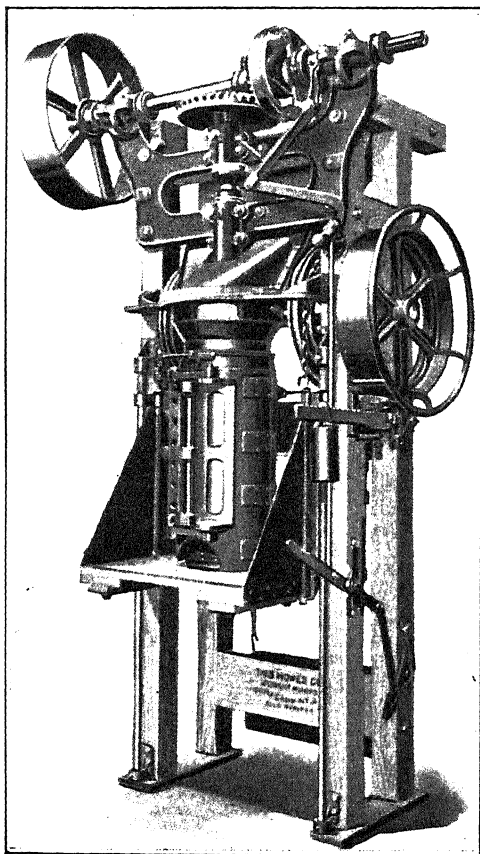
FIG. 245 SECTIONAL VIEW SHOWING WORKING PARTS

FIGS. 244 and 245.—Reel. Barnard & Leas Mfg. Co.

franklinite charge, 1.63 tons coal are required for 2.62 tons ore; for the half/half and dust charge, the figures are 1.36 and 1.95.

The oxide is taken from the baghouse every 24 hr. and transferred to the packing house. Here it is sifted through an 18-mesh brass screen to remove scale and accidental impurities. Vertical, longi-

tudinal and cross-sections of the reel of the Barnard & Leas Mfg. Co., Moline, Ill., are given in Figs. 244 and 245. The length of the screen frame is 6 ft. 3 in., the height 4 ft. 4 in., and the width 2 ft. 3 in.; the reel proper is 5 ft. long and 20 in. in diameter, makes 280 r.p.m. and screens all the oxide that a packing machine can handle—there being provided one reel to a packer.



FIGS. 246.—Mogul packer.

The screened oxide is packed in barrels holding 300 lb. or bags holding 50 lb. by means of a machine which compacts the fluffy product. The Mogul packer (J. Howes & Co., Silver Creek, N. Y.) is shown in two positions in Figs. 246 and 247. Its essential parts are a vertical shaft with propeller at the lower end and bevel gear at the upper, the latter is rotated by a bevel pinion which can be thrown

in and out of gear. The shaft is enclosed by a stationary cylinder open at the bottom and surmounted at the top by a hopper which receives the oxide. The other part is a counter-weighted table which, as seen in the figures, carries a sheet-iron cylindrical housing, made in two sections and provided with hinges and a clamp for the

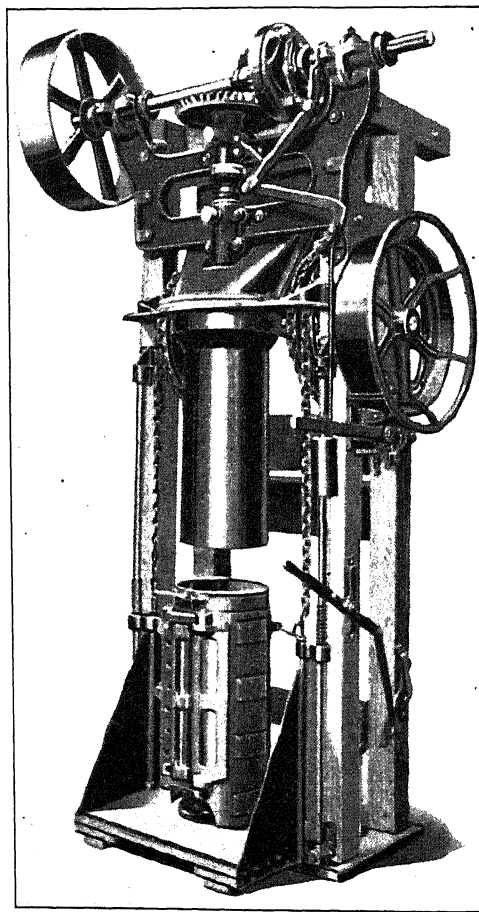


FIG. 247.—Mogul packer.

support of a bag or it forms the support of a barrel. In Fig. 246 the machine is ready for packing, that is the table with the housing holding a bag has been raised to its top position. Zinc oxide is admitted, and the shaft thrown into gear. It revolves, making 260 r.p.m., the propeller compacts the fluffy oxide and pushes down-

ward as the bag is being filled. When full, the shaft is thrown out of gear, the housing opened and the bag removed. The table now sinks to the position shown in Fig. 247, and is ready for another bag. The procedure with barrels is the same as with bags, the housing being replaced by a barrel. The machine packs per hour 6 to 8 bbl. holding 300 lb. oxide, or 30 bags holding 50 lb.

The oxide contains over 99 per cent ZnO ; the principal impurities are SO_3 0.25 to 0.33 per cent, H_2O 0.10 to 0.50 per cent, PbO 0.05 to 0.30 per cent. Analyses of the residuum have been given on page 289.

An important phase in the Eastern type of furnace is that there shall be as little interruption of the operation as possible. With this point in view, also in consideration of the cheapening of the process, the New Jersey Zinc Co. has been experimenting with continuous mechanical furnaces, and has patented¹ a long furnace with traveling grate in which the operation is continuous.² Briquetted coal is charged mechanically to a depth of 6 in. at one end, is ignited by radiated heat and burned by under-grate blast, and the issuing gas carried off. As it travels along, it forms the bed coal and underlies briquetted ore-charge fed continuously to a depth of 3 in. The charge, ignited by the burning bed coal, gives off gases which are withdrawn by a flue. By the time zinc vapors appear, the ignited ore charge has arrived in the chamber which is about 18 ft. long. Under-grate blast furnishes the air necessary. The ignition chamber of coal briquettes is held at 800° to 850°C ., that of ore briquettes at $1,000^\circ$ to $1,050^\circ$, and that of the fuming chamber at $1,100^\circ$ to $1,250^\circ$. The treated ore briquettes retaining their shapes pass off at the tail end of the grate into a grated hopper where part of the fuel ash is screened off. The grate travels at a speed of 7 ft. per minute; the use of ore-fuel briquettes has permitted the reduction of the reducing fuel of the ore charge; a recovery of over 90 per cent of the zinc charged is made.

141. Wetherill Process, West.—The characteristic of Western practice is that oxide ore and roasted blende containing not over 4 per cent S serve as ore and a semi-bituminous coal as fuel; and that while the double furnaces in a block, 8 to 16 in number, have individual air ducts they deliver their dust- and oxide-laden gases into a single overhead flue leading into a combustion chamber, whence, purified in part from deposited dust, they travel through a

¹ U. S. Patent No. 1,322,088-91, 1,322,142-43, Nov. 18, 1919.

² *Chem. Met. Eng.*, 1920, XXII, 330.

cleaning pipe to the fan and the baghouse. The furnaces in a block are worked somewhat independently from one another, but the combined travel of the several products corrects any individual imperfections. The work is thus less rigid than of the Eastern furnace, and is adapted to the varied conditions as regards ore and fuel with which it has to contend.

Figures 248 to 250 represent the Western type of furnace; they give the plan, elevation, and sections of a furnace block of the Western Zinc mining & Reduction Co. at Leadville, Colo.¹ The

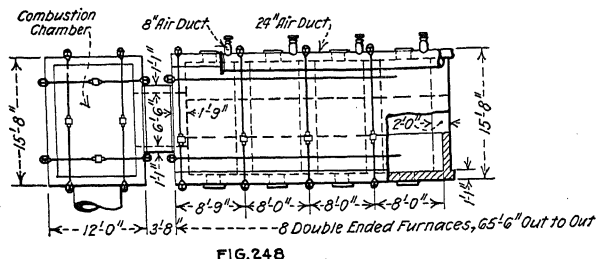


FIG. 248

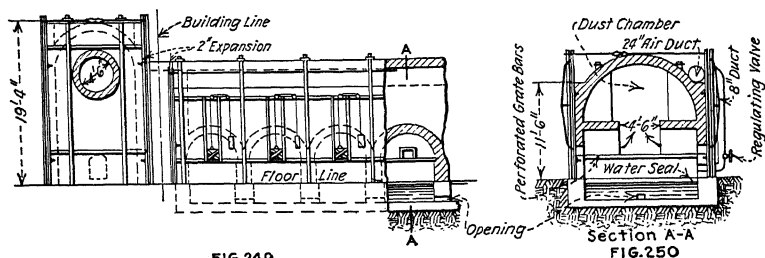


FIG. 249

FIG. 250

FIGS. 248, 249 and 250.—Western type of oxide furnace.

block with eight double furnaces is 65 ft. 6 in. long, 15 ft. 8 in. wide and 11 ft. 6 in. high. A furnace has the usual water basin in the ash pit to prevent the grate bars from buckling. The grate, of the Wetherill type, consists of cast-iron plates 6 ft. 9 in. long, 11 in. wide, $1\frac{1}{4}$ in. thick, with holes $\frac{1}{8}$ in. diameter at the top and $\frac{3}{8}$ at the bottom; two sets of grates, with an area 13 ft. 6 in. by 6 ft. 9 in. — $91\frac{1}{8}$ sq. ft., carry the charges of a double furnace; the ends rest on the furnace wall, at the center they are supported by rails extending across the furnace. In the center of the arch of each double furnace is a flue 4 ft. 6 in. wide which carries the gases into a com-

¹ *Min. Sci. Press*, 1915, CX, 433; *Chem. Met. Eng.*, 1915, XIII, 631; *Eng. Min. J.*, 1917, CIV, 679.

mon semicircular dust chamber and ends in a flue 6 ft. 6 in. wide leading into the combustion chamber, 15 ft. 8 in. by 10 ft. and 19 ft. 4 in. high, whence the gases travel through an overhead brick-lined sheet-iron pipe, 4 ft. 6 in. inner diameter for 30 ft.; at this stage they are sufficiently cooled from the furnace temperature of $1,000^{\circ}\text{C}$. to permit the use of an unlined sheet-iron conduit, 4 ft. in diameter, which is horseshoe shaped (sides 173 ft. 4 in. and 194 ft. long, radius of curve 55 ft.) and leads into a fan delivering into the baghouse. The conduit has discharge gates to remove collected dust. The baghouse has 288 suspended muslin bags, 22 in. in diameter and 24 ft. long; four bags are attached to thimbles of a sheet-iron hopper, the 72 hoppers are arranged in 12 rows and collect from 8 to 10 tons oxide per day. The filtering area is 47,000 sq. ft.; the volume of gas per min. is about 40,000 sg. ft.; this gives an area of 1.2 sq. ft. per cubic foot gas per minute. The bags are shaken by hand every 2 hr, and the hoppers emptied every 24 hr.

The mode of operating is as follows: Supposing the grate to have been cleaned, 100 lb. of bed coal, 50 to a side, are shoveled in, forming a bed about 1 in. thick, and blast is turned on. When the coal burns freely, a charge of 1,000 lb. oxide ore (smithsonite) and 500 lb. coal is given, spread to a thickness of 6 to 8 in., and the blast gradually increased until it registers a maximum of about 5 oz. pressure. The furnace requires no further attention for 6 hr. except that it has to be watched for blow holes. The charge is now rabbled and the blast increased; 1 hr. later the charge is again rabbled, and twice in half-hour intervals, when 8 hr. after charging it is ready to be drawn. In general, the amount of ore charged ranges from 80 to 120 lb. per square foot of grate area, the fuel from 50 to 100 per cent of the weight of the ore; fluxes to the extent of 10 to 90 per cent of the ore may be needed. The best fuel, anthracite, over $\frac{1}{4}$ - and through $\frac{5}{16}$ -in. mesh, is rather high priced; coke may be used and is used, but anthracite and semi-bituminous coals are more common. The furnaces are run in regular order by 12 men working in 8-hr. shifts, 2 men on a side per shift. A block treats 50 tons ore in 24 hr. and produces 6 to 7 tons oxide. The clinker carries 2 to 4 per cent zinc. The oxide contains 95 to 96 per cent ZnO and up to 1.5 per cent Pb ; an analysis gave ZnO 98.0, ZnSO_4 0.5, PbO none, PbSO_4 1.5 per cent.

The works of the Ozark Zinc Oxide Co., Coffeyville, Kan.,¹ treat

¹ Buskett, *Mines & Minerals*, 1907, XXVIII, 193; *Min. Sci. Press*, 1908, XCVII, 604. Editor, *Electrochem. Met. Ind.*, 1908, VI, 305.

sulphide zinc-lead concentrate with not less than 30 per cent metal which is apportioned so as to obtain a mixture with a Zn-Pb ratio of 2:1 and an S-content of 15 to 25 per cent. A plan of the plant is shown in Fig. 251.¹ The mixture is roasted in two five-hearth

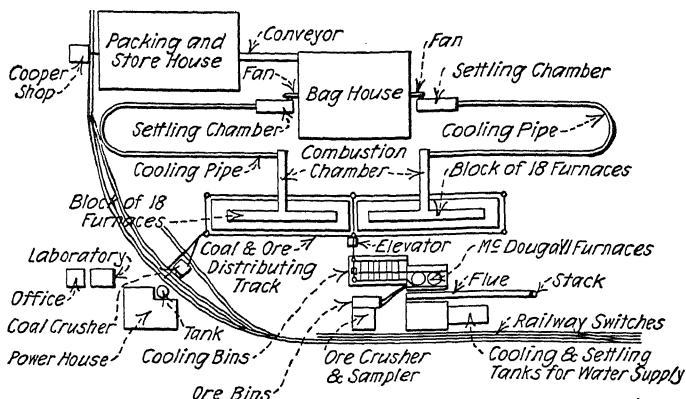


FIG. 251.—Plan of works of Ozark Zinc Oxide Co.

McDougall furnaces, each treating from 20 to 25 tons in 24 hr., which reduce the S-content to 3 per cent. Two blocks of 18 furnaces treat the ore. The 18 double furnaces of a block are similar to those of Leadville; a hearth is 6 by 12 ft.; a cast-iron Wetherill grate, 8 by 72 in. and $1\frac{1}{2}$ in. thick, has holes $1\frac{1}{2}$ in. apart which are $\frac{1}{8}$ in. at top and $\frac{3}{4}$ in. at bottom. Blast is furnished by a 3-ft. fan of the American Blower Co. The fuel is semi-anthracite from Arkansas, crushed to $\frac{1}{2}$ in. The mode of operating is the same as at Leadville except that the charge is frequently rabbled; the gases on leaving the combustion chamber travel through 600 ft. of cooling pipe and pass through a settling chamber, where is placed a 4-ft. suction fan, before they enter the distributing main of the baghouse, which is 90 by 140 ft. From the

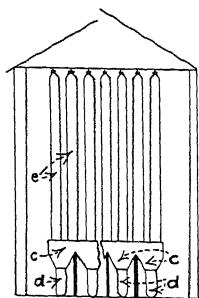


FIG. 252.—Suspension of bags.

main, 18 rectangular branches traverse the baghouse about 8 ft. above the floor, each branch has two rows of thimbles, 25 in a row, to which are tied the bottoms of muslin bags 30 ft. long and

¹ *Min. Sci. Press*, 1908, xcvii, 605.

24 hr. The receiving bags are suspended from the girders above the furnace. The bottom of a bunch has 17 discharge bags, each 24 in. in diameter and 24 in. in length. The bags thus enter the bottoms of the retorts. The retorts are about 24 in. long; the receiving bags are 24 in. long. The plant treated in 24 hr. 65 tons ore which contained 10.5 per cent Ag; the loss in Ag was 1.5 per cent. The loss is lowered by maintaining a low temperature.

A similar plant is the work of the Utah Zinc Co., Murray, Utah.

142. Treatment of Retort Residues. The Western furnace serves for the extraction of lead and lead from retort residues. These contain 10 to 15 per cent Zn, sometimes 10 per cent; about 2 per cent S, and 2 to 4 per cent Pb; or 10 to 15 per cent C.

With 10 to 15 per cent Zn the furnace charges have to be crowded; a space of 24 in. will receive a charge of 3,500 to 3,700 lb., which makes a very small charge. With 10 per cent Zn the charge will weigh 2,000 to 2,500 lb. Crowding the grate of course reduces the yield much, say to 50 per cent; all the lead is completely volatilized. And the S content of a residue containing little Pb this ought to be only 1 per cent, or otherwise the oxide produced will run excessively high in $ZnSO_4$ and contain more SO_2 than is permissible; if the residue contains considerable Pb, over 2 per cent S, perhaps 2 and 4 per cent will do no harm as the S combines with lead as $PbSO_4$.

Residues have been screened through sieves with $\frac{3}{8}$ in. holes to remove the oxide, but the screened oxide has to receive fuel, say 700 lb. of coke or coal to make Pb oxide, so that it is more profitable to treat the residue unscreened.

A furnace ought not to have less than 12 grates, 16 are preferable; a large furnace gives capacity and holds the heat; heat is of vital importance as residue charges have to be run hotter than ore charges.

The treatment of residues is similar to that of ore, except that on account of the greater heat required the blast is more abundant, in fact the charge is crowded with blast. A 12-grate block with 6 in. to a charge will treat 70 tons residue in 24 hr. The clinker in good work always about 1 per cent Zn, and contains only a trace of Pb.

Min. Ind. Press, 1910, 1911, 1912.

The oxide is mostly of poor quality not suited for pigment, it is likely to be sooty which is attributed to the combined presence of silver and cadmium. Residue from Missouri and Wisconsin ore gives a pigment with 6 to 15 per cent PbSO_4 , from Butte ore one with 20 to 35 per cent PbSO_4 , often 2 to 6 per cent ZnSO_4 , and 0.2 to 1.0 per cent SO_2 . Usually the oxide is added to the charges of the spelter furnace, often it is sold to lithopone manufacturers.

The loss in silver depends somewhat upon the presence of NaCl in the residue; if this is absent, from 75 to 80 per cent of the Ag will be found in the clinker, if present nearly all the Ag will be volatilized.

143. Appendix.—As the residues contain their sulphur in sulphide form there is likely to be formed more ZnSO_4 than is permissible in the oxide. In order to correct this, Wemple has patented¹ a process in which he decomposes the salt by mixing with lamp-black and heating in a two-hearth mechanical muffle furnace to $1,100^\circ\text{F}$. ($= 593^\circ\text{C}$.). It will be remembered² that heating ZnSO_4 with an excess of C to 409°C . induces the reaction $2\text{ZnSO}_4 + \text{C} = 2\text{ZnO} + 2\text{SO}_2 + \text{CO}_2$, which becomes energetic at 528°C ., but is slow and not complete, as it is opposed by the reaction $\text{ZnSO}_4 + 2\text{C} = \text{ZnS} + \text{CO}_2$, if the temperature is raised. However, the amount of sulphate is sufficiently reduced to comply with the requirement that the oxide shall not contain over 1 per cent ZnSO_4 and 0.7 per cent SO_2 , and that the combined ZnO and PbO shall exceed 99 per cent.

It has been noted that the oxide produced from silver-bearing residues is likely to contain appreciable amounts of Ag . Such oxide may be used for the production of ZnSO_4 or ZnCl_2 , or for the neutralization and purification of ZnSO_4 solutions formed in leaching roasted Zn-Pb or Zn-Cu ores with H_2SO_4 , preparatory to the electrodeposition of metallic zinc. If this is not feasible, the only way at present is to add it to the oxide of the spelter furnace charges.

In filtering oxide, it has been shown that a large area is required for a comparatively small amount of oxide. At Depue, Ill., G. S. Brooks and L. D. Duncan³ have constructed an automatic filter bag which alternately is inflated and collapsed, shaken while under suction, and given an up- and downward as well as an undulatory motion. They have succeeded in reducing the filtering area of

¹ U. S. Patent No. 1,292,976, Jan. 28, 1919.

² Hofman, *Tr. A. I. M. E.*, 1905, XXXV, 830.

³ *Tr. A. I. M. E.*, 1918, LIX, 218.

2.50 to 3.45 sq. ft. per cubic feet gas per minute of the lead smelter¹ to 0.5 sq. ft. The Allis Chalmers Co., Milwaukee, Wis.,² have placed on the market a dust collector which, while different as regards construction, embodies the principles of Brooks and Duncan.

¹ Eilers, *Tr. A. I. M. E.*, 1912, XLIV, 720.

Hofman, "Lead," 1918, p. 444.

² *Bull.* 1454, January, 1918.

PART II
CADMIUM

CHAPTER X

INTRODUCTION

144. Historical Notice.—Cadmium is probably the first metal that was not discovered in an ore, it was found in a metallurgical by-product. In 1817 Strohmeyer¹ examined a zinc carbonate which had a yellowish tinge; he found no iron, but obtained upon treatment with hydrogen sulphide a yellow precipitate which he thought was arsenic sulphide. Hermann² found the impurity to be a new metal which he named Cadmium.

145. Statistics.—Formerly Belgium and Austria furnished some of the metal; for many years Silesia has been the leading if not the sole producer in Europe. In 1907 the Grasselli Chemical Co. of Cleveland, Ohio, began to produce cadmium from blue powder. In 1919³ there were six operating plants, those of the American Smelting & Refining Co. which started in 1911, the Grasselli Co., Krebs Pigment & Chemical Co., Midland Chemical Co., United States Smelting, Refining & Mining Co. with two plants at Midvale, Utah, which began in 1915, and Kennett, Cal., which began in 1917 (shut down in 1920). These plants appear to meet the demands of the country. The electrolytic zinc plants and manufacturers of lithopone store at present their cadmium-bearing intermediary products. Should there be an increased call for the metal or sulphide, raw material is available to meet this. Table 46 gives the production of metallic cadmium and sulphide in the United States and Germany during the years 1906 to 1919.

146. Bibliography.⁴—The treatises by Ingalls, Lodin and Liebig noted on page 7, treat of cadmium; nearly all publications dealing with zinc discuss some phases of cadmium. There exist three publications dealing with cadmium alone, one is by E. Jensch, "Das Cadmium, sein Vorkommen, seine Darstellung und Verwendung," Enke, Stuttgart, 1898; another by G. Juretzka, "Ueber Rohmaterialbeschaffung, Technik und Rentabilität bei der metallurgischen Cadmiumgewinnung," *Metall. u. Erz*, 1915, XII, 235; Trans. by O. C. Ralston, *Met. Chem. Eng.*, 1917, XVI, 146; the third by H. R. Hanley, "Production of Electrolytic Cadmium," *Chem. and Metall. Eng.*, 1920, XXIII, 1257.

¹ *Schweigg, J.*, 1817, XXI, 297.

² *Gilb. Ann.*, 1818, LIX, 95.

³ Siebenthal, *Min. Res. of the U. S.*, 1919, I, 1.

⁴ *Min. Res. U. S.*, 1919, I, 12.

TABLE 46.—METALLIC CADMIUM AND CADMIUM SULPHIDE PRODUCED IN THE UNITED STATES AND GERMANY, 1906-1920

Year	United States					Germany		
	Metallic cadmium		Cadmium sulphide			Metallic cadmium		
	Quantity (pounds)	Value based on sales	Average price per pound	Quantity (pounds)	Value based on sales	Average price per pound	Quantity (pounds)	Value
1906	300	\$300	\$1.00	(a)			47,368	\$36,083
1907	14,000	14,350	1.025	(a)			72,039	60,757
1908	8,000	6,000	0.75	(a)			72,741	48,590
1909	5,300	2,783	0.525	(a)			81,982	46,777
1910	4,700	2,585	0.55	(a)			96,316	39,309
1911	26,152	17,566	0.67	2,392	\$1,674	\$0.70	93,861	53,372
1912	52,508	30,875	0.76	8,998	6,400	0.71	94,262	63,507
1913	54,108	41,838	0.77	17,302	12,136	0.70	81,993	63,641
1914	(b) 51,409	81,205	0.89	22,723	20,241	0.89	(c) 86,000	
1915	91,415	108,443	1.19	10,624	12,057	1.13	(c) 82,000	
1916	135,212	210,931	1.56	22,176	27,042	1.26	(c) 128,000	
1917	207,408	305,097	1.47	50,169	70,939	1.41	(c) 172,000	
1918	127,164	188,203	1.48	51,702	70,315	1.36	(c) 236,000	
1919	90,939	121,026	1.22	31,197	37,436	1.20	(c) 85,395	
1920	129,283	151,261	1.17	32,133	37,274	1.16	(d)	
	1,046,988	1,292,363		249,416	296,414			

(a) No production.

(b) Exclusive of 4,225 lb. of cadmium in residues sold for export.

(c) Statistics of production and average selling price for 1914-1919 from *Glückauf*, vol. 56, pp. 818-819, 1920. The value is expressed in marks because the exchange value of the mark is not available for part of the period.

(d) Figures not available.

CHAPTER XI

PROPERTIES OF CADMIUM

Cadmium is closely related to zinc; physical and chemical changes with cadmium occur at lower temperatures than with zinc.

147. Physical Properties.—The metal has a tin-white color and metallic luster, takes a fine polish; the specific gravity of cast metal is 8.6040, which is increased to 8.6944 by hammering;¹ it crystallizes in hexagonal pyramids. Figure 253² shows hexagonal dendrites from the surface of an ingot cast in an iron mold. According to Gettman³ there exist two allotropic modifications, Cd stable below

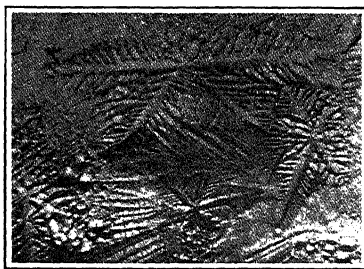


FIG. 253.—Crystals of cadmium.

37.5°C., and Cd stable above this temperature. The investigations of Cohen-Heldermann⁴ and Jänecke,⁵ are of interest in this connection. The metal shows no cleavage, the texture is compact, the fracture brilliant and crystalline, but fine-grained and dull when impure; it is soft, tranishes paper, can be cut with a knife, is harder than tin and softer than zinc, standing between tin and gold; is malleable and ductile, can be readily rolled and hammered into foil and drawn into wire; on bending it gives a crackly noise similar to tin when pure; this is not the case with impure metal; at 80°C. it be-

¹ Strohmeyer, *Schweigg. J.*, 1818, XXII, 362.

² Campbell, Sixth Report Alloys Research Committee, 1901, Appendix; *Metallurgie*, 1907, IV, 825.

³ *J. Am. Chem. Soc.*, 1917, XXXIX, 1806.

⁴ *Zt. Chem.*, 1914, LXXXVII, 409; 1914-15, LXXXIX, 493, 728.

⁵ *Op. cit.*, 1915, XC, 257, 313.

comes so brittle that it may be pulverized; it is stronger than zinc standing between tin and gold, the tensile strength is 13,660 lb. per square inch, the elongation 44 per cent in 3 in. It melts at $321.7^{\circ}\text{C}.$,¹ boils at $778^{\circ}\text{C}.$ ² as a yellowish-brown vapor. The mean specific heat³ between 0° and t° is $0.0546 + 0.000012 t$; the quantity of heat to bring from 0° to melting point ($321^{\circ}\text{C}.$) is 18.8 cal.; the latent heat of fusion 13.0 cal., hence, the quantity of heat at melting point $18.8 + 13.0 = 31.8$ cal.; the specific heat of liquid metal is 0.0623. The quantity of heat in metal at boiling point ($780^{\circ}\text{C}.$) is 60.3 cal.; the latent heat of vaporization is 251 cal. (calculated), hence, the quantity of heat in vapor at 780° is $60.3 + 251 = 311.3$ cal. The specific heat of vapor is 0.225 (assumed) per cubic meter and 0.045 (calculated) per kilo. The vapor tension, p , liquid is $\log. p = -\frac{6151}{T(\text{absolute})} + 8.74$; at melting point $= 2.6 \times 10^{-2}$ mm. Hg; solid is $\log p = -\frac{6470}{T(\text{absolute})} + 9.28$; at $0^{\circ}\text{C}.$ $= 38 \times 10^{-15}$ mm. Hg. The thermal conductivity per cubic m. per degree per second is 0.22 g. cal. The linear expansion coefficient at 0° to $100^{\circ}\text{C}.$ is 0.0000306. The specific resistance at $0^{\circ}\text{C}.$ is 6.2 to 7.0 microhm per cm.³

Cadmium is diamagnetic.

148. Chemical Properties.—The atomic weight is 112.4. The metal is not attacked by dry air, by moist air it is oxidized superficially becoming coated with a grayish-white film, at red heat it burns to yellowish-brown CdO. It does not decompose water at $100^{\circ}\text{C}.$; Cd vapor decomposes steam forming CdO and H; it is oxidized by heating with niter and alkali carbonate. Cadmium is readily soluble in HCl, H_2SO_4 , especially in HNO_3 , slowly in acetic acid (CH_3COOH); it forms double salts with similar salts of K, Ca, Mg, etc. It is precipitated from solutions by Zn. Soluble Cd salts are poisonous.

¹ Holborn-Day, *Drud, Ann.*, 1900, II, 505.

² Berthelot, *Compt. rend.*, 1900, CXXXI, 384.

³ Richards, J. W., "Metallurgical Calculations," McGraw-Hill Book Co. Inc., New York, 1918, Part I, p. 93.

CHAPTER XII

CADMIUM OF COMMERCE, ITS IMPURITIES AND THEIR EFFECTS

149. General.—Cadmium is sold in the form of small sticks $\frac{1}{16}$ to $\frac{1}{8}$ in. in diameter. As a rule it is very pure; formerly 2 per cent impurity was allowed, today (the Silesian standard) it contains less than 0.5 per cent foreign matter, impurities are traces of Zn, Fe, Sn, Pb, Cu, Ni, Tl. Jensch¹ gives a sample of Kunigunde works containing 99.8 Cd and 0.005 Fe; another Silesian brand as 99.65 Cd and 0.01 Fe. An analysis of the metal of the American Smelting & Refining Co. shows Cd 99.839, Cu 0.005, Pb 0.040, As 0.009, Zn 0.100, Fe 0.021, S 0.005 per cent; one of the United States Smelting, Refining & Mining Co., Cd 99.75, Cu none, Pb 0.03, As none, Sn none, Zn 0.18, Fe none, S not det.; one of the Grasselli Chemical Co., Fe 0.005, Cu 0.05, Zn 0.01, Pb 0.32, Cd (by difference) 99.61, Cd (determined) 99.47.

Zinc makes the metal brittle.² The curve Cd-Zn has been given in Fig. 3. The effects of small amounts of impurities on cadmium do not appear to have been studied. The following freezing-point curves have been published in the technical literature: Cd-Ag,³ Cd-Al,⁴ Cd-As,⁵ Cd-Au,⁶ Cd-Bi,⁷ Cd-Ca,⁸ Cd-Co,⁹ Cd-Cr,¹⁰ Cd-Cu,¹¹

¹ *Op. cit.*, p. 220.

² Glasunoff-Matweeff, *Internat. Zt. Metallogr.*, 1914, V, 113.

³ Petrenko-Fedorow, *Zt. Anorg. Chem.*, 1911, LXX, 161.

Carpenter *Internat. Zt. Metallogr.*, 1912, III, 170.

⁴ Gwyer, *Zt. Anorg. Chem.*, 1908, LVII, 150.

⁵ Schemtschuschny, *Internat. Zt. Metallogr.*, 1913, IV, 228.

⁶ Vogel, *Zt. Anorg. Chem.*, 1906, XLVIII.

Saldau, *Internat. Zt. Metallogr.*, 1915, VII, 3.

⁷ Kapp, *Dissertation*, Königsberg, 1901.

Stoffel, *Zt. Anorg. Chem.*, 1907, LIII, 149.

Portevin, *Rev. Metallurgie*, 1907, IV, 389.

Petrenko-Fedoroff, *Internat. Zt. Metallorg.*; vi, 212.

⁸ Donski, *Zt. Anorg. Chem.*, 1908, LVII, 196.

⁹ Lewkonja, *op. cit.*, 1908, LIX, 322.

¹⁰ Hindrichs, *op. cit.*, 1908, LIX, 427.

¹¹ Sahmen, *op. cit.*, 1906, XLIX, 305.

Cd-Fe,¹ Cd-K,² Cd-Li,³ Cd-Mg,⁴ Cd-Pb,⁵ Cd-Sb,⁶ Cd-Se,⁷ Cd-Sn,⁸
Cd-Te,⁹ Cd-Tl,¹⁰ Cd-Bi-Zn,¹¹ Cd-Bi-Pb.¹²

¹ Isaak-Tammann, *op. cit.*, 1907, IV, 61.

² Smith, *op. cit.*, 1908, LVI, 121.

³ Masing-Tammann, *op. cit.*, 1910, LXVII, 196.

⁴ Boudouard, *Berg. Hüttenm. Z.*, 1903, LXII, 64.

⁵ Kapp, Dissertation. Königsberg, 1901.

Stoffel, *Zt. Anorg. Chem.*, 1907, LIII, 152.

⁶ Treitschke, *op. cit.*, 1906, I, 217.

Kurnakow-Konstantinoff, *op. cit.*, 1908, LVIII, 16.

⁷ Chikashige-Hitosaka, *Mem. College Science, Kyoto*, 1917, II, 233.

⁸ Kapp, Dissertation, Königsberg, 1901.

Stoffel, *Zt. Anorg. Chem.*, 1907, LIII, 146.

Bucher, *op. cit.*, 1916, XCVIII, 197.

Schleicher, *Internat. Zt. Metallogr.*, 1912, II, 76.

⁹ Kobayashi, *Zt. Anorg. Chem.*, 1911, LXIX, 4.

¹⁰ Kurnakow-Puschin, *op. cit.*, 1902, XXX, 106.

¹¹ Mathewson-Scott, *Internat. Zt. Metallogr.*, 1913, V, 1.

¹² Barlow, *Zt. Anorg. Chem.*, 1911, LXX, 178.

CHAPTER XIII

INDUSTRIAL USES AND ALLOYS

150. General.—Cadmium is used very little unalloyed, it is a constituent of many fusible alloys,¹ and serves for the preparation of amalgams and cadmium sulphide, and of its salts which are used in the arts, in medicine, and in electro-plating.

Some fusible alloys, that is alloys having a lower melting point than tin, containing cadmium are given in Table 47.² While bismuth

TABLE 47.—FUSIBLE ALLOYS CONTAINING CADMIUM

Name	Parts by weight				Melting point	
	Cd	Pb	Sn	Bi	Degrees, Centigrade	Degrees, Fahrenheit
Lipowitz metal.....	3	8	4	15	70.0	158
Wood's metal.....	2	4	2	5	60.0-71.1	140-160
Fusible alloy.....	2	11	3	16	76.7	170
Fusible alloy.....	10	4	3	8	75.0	167
Fusible alloy.....	1	..	2	3	95.0	203
Fusible alloy.....	1	..	3	5	95.0	203
Fusible alloy.....	1	..	1	2	95.0	203
Fusible alloy.....	1	2	1	4	65.5	150
Fusible alloy.....	2	2	4	..	86.1	187
Electrical cut-off.....	15	20	21	50		

which forms a part of most fusible alloys is likely to make the alloy brittle, cadmium usually renders it more malleable and ductile.

Cliché metal for stereotype plates consists of 50 Pb, 27.5 Sn, and 22.5 per cent Cd; it is said to be superior to the corresponding bismuth cliché metal.

Cadmium-silver alloys with as much as 25 per cent cadmium are used in silver plating. Alloys of cadmium and silver with some copper which are white are used by jewelers in the form of plate and wire. They contain Ag 98-50, Cu 1.5-5.0, and Cd 0.5-45.0 per cent.

¹ Parravano-Sirovich, *Gazetta chim. ital.*, 1912, XLII¹, 360; *J. Inst. Metals*, 1912, VIII, 322.

² Siebenthal, *Min. Res. U. S.*, 1908, 1, 800.

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Cadmium dental amalgam¹ consists of 26 per cent cadmium and 74 per cent quicksilver; tin or bismuth are frequently added to render the amalgam more pliant under heat. Palladium has replaced cadmium to a certain extent in dentistry.

Cadmium has been used in the first three-quarters of 1918 as a partial substitute for tin in solders.² In Germany, where tin was very scarce during the war, but cadmium abundant, solders ranging from 10 per cent Sn and 10 per cent Cd to 2 per cent Sn and 30 per cent Cd were used.³

Touceda⁴ patented alloys of lead and cadmium to be used as bearing metals, they contain 97.25-82.00 per cent Pb and 2.75-18.00 Cd.

¹ Curve by Bijl, *Zt. phys. Chem.*, 1902, XLI, 641.

² Siebenthal, *Min. Res. U. S.*, 1918, I, 9; 1919, I, 1.

³ Siebenthal, *Tr. A. I. M. E.*, 1919, LX, 185.

⁴ *Brass World*, 1908, IV, 352.

CHAPTER XIV

CADMIUM COMPOUNDS

151. Cadmium Oxide, CdO (87.5 per cent Cd, $112 \text{ Cd} + 16 \text{ O} = 128 \text{ CdO} + 66,300 \text{ cal.}$).—It has been found at Monteponi, Sardinia;¹ it is prepared by burning Cd, by calcining CdCO_3 , $\text{Cd}(\text{NO}_3)_2$, H_2CdO_2 ; is a dark-brown infusible powder. Its volatilization is noticeable at 700°C. ,² parallel tests showed that zinc oxide began to be volatilized at $1,000^\circ\text{C.}$ It attracts CO_2 from the air, is a strong base, is readily reduced to metal by CO and C; reduction by C begins at about 600°C. ,³ reduction of ZnO in parallel tests was noticeable at 950°C. Thus experimental evidence is furnished that CdO is volatilized and reduced at lower temperatures than ZnO. Johnson⁴ gives a range of temperature of 772° to 813°C. for the reduction of CdO by charcoal and coke.

Cadmium Hydroxide, H_2CdO_2 , is a white amorphous powder that is obtained by precipitation from salt solution with alkali. It is soluble in NH_4O , insoluble in HKO , HNaO , $(\text{NH}_4)_2 \text{CO}_3$, loses H_2O at 300°C.

152. Cadmium Sulphide, CdS (77.7 per cent Cd, $112 \text{ Cd} + 32 \text{ S} = 144 \text{ CdS} + 34,400 \text{ cal.}$), occurs as greenockite on blende. It is prepared in the dry way as a yellow substance by heating Cd and S, preferably by heating CdO and S; in the wet way by precipitating from sulphate or chloride solution. There exist two modifications, a yellow having a specific gravity 3.906 and a red one of 4.513.⁵ The color of the precipitate varies from light-to dark-yellow or orange-yellow according to the method of precipitation; a light-yellow precipitate is obtained from a 10-per cent sulphate or chloride solution until half of the cadmium has been converted into CdS, the H_2S being admitted a little beneath the surface of the solution.

¹ *Chem. Z.*, 1901, XXV, 561.

² Doeltz-Graumann, *Metallurgie*, 1906, III, 372.

³ Doeltz-Graumann, *Metallurgie*, 1914, IV, 419.

⁴ *Tr. A. I. M. E.*, 1914, XLVII, 277.

⁵ Buchner, *Chem. Z.*, 1887, XI, 1,087, 1,107

Klobukow, *J. prakt. Chem.*, 1889, XXXIX, 413.

The precipitate is dark-yellow if all the cadmium is thrown down from a warm solution that is being shaken; it is orange-yellow when completely separated from a boiling 2-per cent chloride solution containing 5 per cent HCl.

It is non-volatile, dissociated below 600°C., and decomposed by roasting. It is soluble in concentrated HCl, with difficulty in dilute HCl even when hot; it is soluble in HNO₃ with difficulty in H₂SO₄.

153. Cadmium Sulphate, CdSO₄ (54 per cent Cd; 112 Cd + 32 S + 64 O = 208 CdSO₄ + 219,900 cal., in dilute solution 231,600 cal.).—The hydrous salt 3CdSO₄ + 8H₂O is the principal form, there exist others. It is prepared by dissolution of Cd or CdO in H₂SO₄, is a whitish salt, crystals are colorless, loses its water at 170°C. and its SO₃ at 890°.¹ Its solubility in water is given in Table 48 and its solubility in aqueous solutions of sulphuric acid in Table 49.² Electric conductivity according to Grottrian is given in Table 50.³ The e.m.f. of 2.03 volts is required to decompose CdSO₄ into Cd and SO₄, while that for ZnSO₄ is 2.35.

TABLE 48.—SOLUBILITY OF CADMIUM SULPHATE IN WATER

Degrees Centigrade	Grams CdSO ₄ per 100 g.		Solid phase
	Solution	Water	
0.0	43.01	76.48	CdSO ₄ · $\frac{8}{3}$ H ₂ O
10.0	43.18	76.00	CdSO ₄ · $\frac{8}{3}$ H ₂ O
20.0	43.37	76.60	CdSO ₄ · $\frac{8}{3}$ H ₂ O
40.0	43.99	78.54	CdSO ₄ · $\frac{8}{3}$ H ₂ O
60.0	44.99	83.68	CdSO ₄ · $\frac{8}{3}$ H ₂ O
73.5	46.6	87.28	CdSO ₄ · $\frac{8}{3}$ H ₂ O
74.5	46.7	87.62	CdSO ₄ ·H ₂ O
77.0	42.2	73.02	CdSO ₄ ·H ₂ O
85.0	39.6	65.57	CdSO ₄ ·H ₂ O
90.0	38.7	63.13	CdSO ₄ ·H ₂ O
100.0	37.8	60.77	CdSO ₄ ·H ₂ O

¹ Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 563.

² Seidell, A., "Solubilities of Inorganic and Organic Compounds," Van Nostrand, New York, 1919, pp. 178, 179.

³ Landolt-Bernstein-Roth, "Physikalisch-chemische Tabellen," Springer, Berlin, 1912, p. 1,096.

TABLE 49.—SOLUBILITY OF CADMIUM SULPHATE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 0°C.

Equivalents per 10 g. H ₂ O		Density of solutions	Grams per 100 g. H ₂ O	
H ₂ SO ₄	CdSO ₄		H ₂ SO ₄	CdSO ₄
0.0	71.6	1.609	0.00	74.61
3.87	70.9	1.591	1.90	73.87
12.6	62.4	1.545	6.18	65.03
28.1	50.6	1.476	13.78	52.73
43.3	40.8	1.435	21.23	42.52
47.6	37.0	1.421	23.34	38.56
53.8	32.7	1.407	26.38	34.07
71.5	23.0	1.379	35.06	23.96

TABLE 50.—ELECTRIC CONDUCTIVITY OF CADMIUM SULPHATE SOLUTIONS

CdSO ₄ per cent	Per cubic centimeter in reciprocal ohms at 18°C.
1	41.6
5	146.0
10	247.0
15	325.0
20	388.0
25	430.0
30	436.0
35	424.0
36	421.0

CHAPTER XV

CADMIUM ORES

154. General.—The only recognized cadmium mineral is greenockite, CdS , with 77.7 per cent cadmium, which is honey-colored, citron-yellow to orange-yellow, lustrous, and has an orange-yellow streak. No greenockite deposits have as yet been discovered. Cadmium is found with sulphide and oxide zinc ores as sulphide and carbonate. According to Jensch,¹ Silesian zinc ores contain 0.102 per cent Cd; Waring² gives the average Cd content of Joplin ores as 0.358; his figures for 1902–1916³ tell a similar story. Ores in the district extending from Miami, Okla., to Waco, Mo., contain double the amount Cd as do those from Joplin. In general it may be said that the cadmium in zinc ores is present in the ratio of 1Cd: 200 Zn.

The sources of cadmium that are being utilized as raw material for metallurgical treatment are blue powder from zinc retorts, baghouse fume from lead blast furnaces, residues from the purification tanks of electrolytic zinc refineries, and residues from lithopone plants. In Europe blue powder is the main source of cadmium, in the United States baghouse fume and possibly lithopone residues; the copper-cadmium precipitate of electrolytic zinc plants is stored for the present.

Blue powder from Silesian muffles collected during the first 2 hr. of distillation averages 6 per cent Cd, that collected later averages 1.2 to 2 per cent Cd.⁴ The Dagner condenser, Figs. 172 to 174, through which the dust passes gathers a material which averages 3 to 4 per cent Cd. Belgian blue powder contains according to Firket⁵ 0.52, 1.30, 1.80 per cent Cd. Blue powder from the United States may be said to average about 2 per cent Cd.

Baghouse flue dust from lead blast furnaces contains at first only traces of Cd; this dust burnt in the cellars of the baghouses is

¹ *Op. cit.*, p. 204.

² *J. Am. Chem. Soc.*, 1904, XXVI, 16.

³ *Tr. A. I. M. E.*, 1917, LVII, 660.

⁴ Jensch, *op. cit.*, 212.

⁵ *Ann. Min. Belg.*, 1911, VI, 52.

returned to the blast furnaces, the process is repeated, maybe for several years as the concentration is a very gradual process, until it becomes unprofitable to smelt the arsenical fume on account of the low content in lead and the high tenor in cadmium. Assays for more or less concentrated dust from lead blast furnaces at Leadville contained 5.5, Pueblo 5.1 and 7.0, Durango 1.4, Murray 5.05, Midvale 0.02 per cent Cd. While in the process of concentration arsenic may be removed at intervals by passing the dust through a Brunton furnace. A sample of enriched dust contains *e.g.*, Cd 44.00, As 23.00, Pb 12.00, Al 4.40, Fe 0.90, Cu 0.03, Cl 1.20 per cent, and Ag 1.00 and Au 0.01 oz. per ton.

The Cd-Cu precipitate from electrolytic zinc refineries contains about 12 per cent Cd; it is mostly stored for the present. The residues from lithopone plants contain about 8 per cent Cd; the raw material is an impure oxide of zinc from which the zinc has been dissolved by acid.

CHAPTER XVI

METALLURGICAL TREATMENT OF CADMIUM ORES

155. General.—Dry and wet methods are used for the recovery of cadmium from its ores. The dry method is fractional distillation of blue powder. The wet method uses as raw material a concentrated flue dust with about 10 per cent Cd; this is subjected to a preliminary treatment with sulphuric acid to render cadmium soluble in H_2SO_4 ; from the cadmium solution, after it has been purified, the cadmium is precipitated either by zinc or by electrolysis.

156. Fractional Distillation.—The separation of CdO from ZnO by fractional distillation is based upon the fact that CdO is more readily reduced to metal than ZnO, and that Cd is volatilized at a lower temperature than Zn. The reduction of CdO is noticeable at 700°C ., of ZnO at 950°C . Practical figures for CdO¹ are 702° to 813°C . and for ZnO 1,022 to $1,088^\circ$. The boiling point of Cd is 778°C . and of Zn 920° . There is therefore a range of temperature of about 200°C . in which the process has to be carried on. If a mixture of CdO and ZnO, charged with the necessary fuel, is distilled in a retort within the given range of temperature, the Cd vapor will pass off into the condenser before the Zn, and will be collected separately as a blue powder or oxide charged with more Cd than Zn. The operation will have to be repeated before one can proceed to the final distillation, when Cd metal, still to be refined, is obtained. The losses in the process are tremendous. In a test at the Kunigunde works, Silesia,² with 592 lb. blue powder averaging 84.2 per cent Zn, 5.3 Pb, 4.1 Cd there was a recovery of 31.26 per cent cadmium; at Engis, Belgium,³ with blue powder assaying 1.5 to 1.6 per cent Cd there was a recovery of 30.12 metal.

At Engis, Belgium,⁴ blue powder and oxide containing 1.5 to 1.6 per cent Cd were formerly⁵ mixed with fine coal, distilled in 12 hr. in a Belgian furnace having 15 cast-iron retorts, three rows of five each,

¹ Johnson, *Tr. A. I. M. E.*, 1914, xlvii, 227.

² Jensch, *op. cit.*, p. 216.

³ *J. prakt. Chem.*, 1864, xci, 359; *Berg. Hüttenm. Z.*, 1864, xxiii, 368.

⁴ *Loc. cit.*

⁵ Cd is no longer produced in Belgium.

with cast-iron condensers; in the mouth of the retort is placed some coal, the mouth of a condenser is closed with a wooden plug having a central bore, over the mouth of the condenser is slipped a sheet-iron prolong. The ore charge goes into the two lower rows and is distilled in 12 hr. the retorts being held at a dark-red; 100 lb. of dust give 13 lb. of enriched dust with 6 per cent Cd which is pretty free from Zn; it is mixed with coal and distilled in the upper row of retorts. During the distillation of the enriched dust, metallic cadmium is drawn every hour. Three grades of metal result, pure metal (53 per cent), 75-per cent metal (18 per cent), and 40-per cent metal (29 per cent). The impure grades are refined by frac-

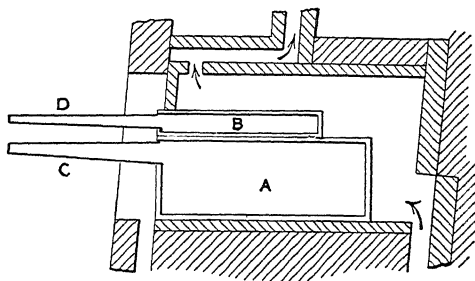


FIG. 254.—Silesian retort for cadmium.

tional distillation. Of the total cadmium there are recovered, as stated above, as metal 30.12 per cent, 21.27 per cent remain in the residue, and 48.71 per cent are lost by volatilization.

At the Wilhelmine works, Upper Silesia, which furnish two-thirds of the product of that province which means for that time two-thirds of the world's product, the muffles shown in Fig. 254¹ are used. The muffle, *A*, 70.87 in. long, is held at a dark-red; it is charged with about 250 lb. oxide containing 3 to 4, sometimes 5 per cent Cd, and 15 per cent coke. The distillation lasts 22 hr.; the reduced cadmium is collected in the sheet-iron condenser, *C*, partly as metal, partly as oxide. The metal is pure enough to require only re-melting before casting into sticks. The powder is collected and distilled every third day in the smaller muffle, *B*, at a higher temperature than that prevailing in *A*. The metal collected in the condenser, *D*, is 99.5 per cent pure and is cast as is that obtained from *C*. The residue from retort, *A*, is returned to the zinc distillation furnace.

¹ Ingalls, *Min. Ind.*, 1898, VII, 750.

At the Hohenlohe works, Upper Silesia,¹ the cadmium-bearing oxide is distilled at a low temperature in muffles provided with prolongs. A muffle is charged with 110 lb. oxide and 600 lb. reducing fuel. The enriched product, consisting of metallic and oxidized cadmium, is mixed with equal parts of charcoal, and distilled in charges of 17 lb. in cast-iron retorts which are lined with muffle mixture and closed with a wooden plug over which is slipped a wrought iron prolong. A charge of 110 lb. oxide furnishes 13 lb. of cadmium which, melted in an iron crucible under a cover of tallow, gives 11 lb. refined metal containing Cd 99.3 to 99.6 per cent, Zn 0.03 to 0.04, Fe 0.02, Pb 0.15.

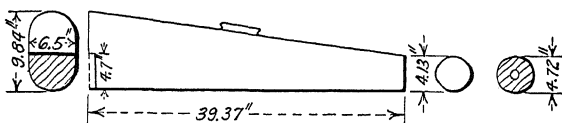


FIG. 255.—Sheet iron condenser for retort.

Modern practice (probably Silesian) is discussed by Juretzka.² The zinc dust (blue powder and oxide) is mixed with 50 per cent of its weight of carbon and distilled at a dull-red heat for 22 hr. in a furnace that is usually used for zinc oxide. A conical sheet-iron condenser, shown in Fig. 255, is recommended to collect the dust; it is white-washed at first, a coating of oxide which forms later serves the same purpose, for the protection of the walls. At the close of the distillation period the condenser is removed, cooled in water, and emptied. The concentrated dust contains about 75 per cent Cd, it is grayish-white and feels soft and greasy; if it is hard and dry, the furnace temperature had been too high and zinc had been distilled. In such a case the zincky parts can be brought to the top by shaking the box into which the dust had been emptied, and removed by skimming; the skimmings are added to a subsequent charge. The residue from the retort contains 40 to 50 per cent Zn and goes to the zinc-distilling furnace.

The concentrated zinc dust is mixed with 40 per cent charcoal or 60 per cent high-grade coke, moistened, and charged into a cast-iron retort shown in Fig. 256, leaving the front part empty for the collection of molten cadmium. The retort is heated in a small

¹ Schmieder, *Oest. Jahrb.*, 1889, XXXVII, 404.

² *Metall u. Erz*, 1915, XII, 235; transl. by Ralston, *Met. Chem. Eng.*, 1917, XVI, 146.

reverberatory furnace having an ordinary grate. The sheet-iron condenser, shown in Fig. 257, is shoved into a retort when distillation begins and luted. As the exit opening of the condenser is small, 0.39 in., the gases, generated at first, issue quickly and are

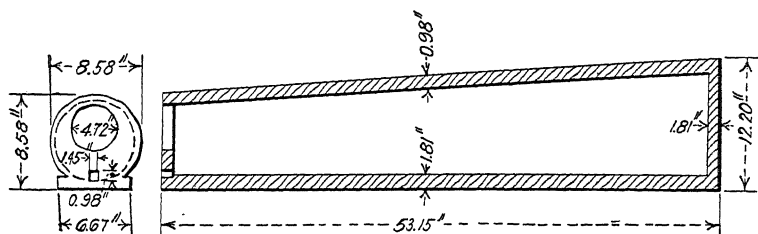


FIG. 256.—Cast iron retort.

likely to break the lute which has to be mended, as it is essential to keep out all air. During the distillation, which lasts 24 hr., cadmium collects at the front of the retort and is removed every 4 hr. with an iron ladle. The temperature is a dull-red, as if higher, zinc would come over. Every 10 hr. the condenser is taken off to

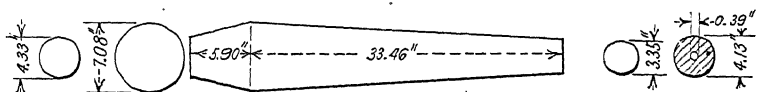
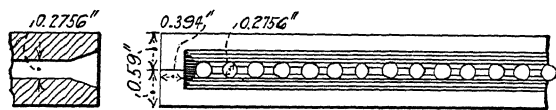


FIG. 257.—Sheet iron condenser for retort.

remove any cadmium that had collected in it. While the condenser is being emptied the mouth of the retort is temporarily closed with a brick. The metal collected in the condenser which is shot through with needle-shaped crystals, is returned to the retort. In the 30 min. it takes to clean the condenser, the contents of the



FIGS. 258 and 259.—Cadmium mold.

retort are stirred, as they have a tendency to cake. The crude cadmium is melted in a cast-iron kettle under a cover of oil and cast into sticks in a mold shown in Figs. 258 and 259, furnishing sticks 0.27 in. in diameter and 9.84 in. long, after the gate has been

cut off with shears. For the purification of medium grade metal, the impure metal is placed at the back of a warmed retort, a dam of sand built in front of it, and the purified metal collected in the front and the condenser.

157. Wet Processes. General.—The solution of cadmium oxide in acids and the precipitation of cadmium either chemically or electrolytically have been recommended by metallurgical chemists.

For instance Rigg patented a process¹ for the removal of cadmium from oxide zinc ore by leaching with just enough sulphuric acid to remove the cadmium which dissolves in preference to the zinc. Earlier tests made by Palmer² with Joplin blends were unsatisfactory.

In flue dust from blende roasting furnaces assaying 0.22 to 1.64 per cent Cd, Jensch³ found, however, that 40 per cent of the cadmium was water soluble.

Flue dust has been treated with dilute sulphuric acid and cadmium sulphide precipitated with hydrogen sulphide; the CdS contaminated, with As_2S_3 , is freed from arsenic by a slight roast, leaving behind brown CdO, rich material for the preparation of cadmium salts.

Lithopone factories have $CdCl_2$ in their raw $ZnCl_2$ solutions, the cadmium is precipitated by means of blue powder.

Blue powder has been treated with HCl, zinc going into solution in preference to cadmium, leaving a residue of cadmium and lead; some cadmium that went into solution being re-precipitated by means of blue powder. The residue rich in cadmium is distilled.

Electrodeposition of cadmium is reviewed by Cowper-Cowles⁴ and by Mathers and Marble⁵ who add their own experimental work.

Stevenson⁶ developed a process for treating baghouse dust. The material is dead roasted, pulverized and leached with sulphuric acid; the acid solution is electrolyzed with a current of 1.8 to 2.1 volts until the copper, bismuth, etc., have been removed, then the cadmium is deposited with a current of 1.5 to 7.2 amp. per square foot and a voltage of 2.2 to 3.4. The process was installed at Midvale, Utah, but has been abandoned.

In this connection it is to be noted that Smith and Fränkel⁷

¹ *Eng. Min. J.*, 1915, XCIX, 659; U. S. Patent No. 1,129,904, Dec. 3, 1914.

² *Min. Res. U. S.*, 1908, I, 798.

³ *Op. cit.*, p. 212.

⁴ *Electrochemist & Metallurgist*, 1903-4, III, 582.

⁵ *Tr. Am. Electrochem. Soc.*, 1914, XXV, 297, 319.

⁶ *Min. Eng. World*, 1916, XLV, 661; *Min. Ind.*, 1916, XXV, 89.

⁷ *Ber. deutsch. Chem. Gesellsch.*, 1884, XVII, 1,611.

found that from a sulphate copper-cadmium solution containing sulphuric acid, no cadmium was deposited with a current of 0.03 amp. per square centimeter or 0.03 amp. per square foot cathode area.

Borchers¹ in the electrolysis of impure cadmium with an electrolyte of CdCl_2 or CdSO_4 found that a current of 6 to 15 amp. per square foot at an e.m.f. of 2.8 to 3.15 volts did satisfactory work.

158. Treatment of Flue Dust. General.—Analyses of the raw material are given in §§154, 160. The treatment involves, rendering soluble the cadmium by the aid of sulphuric acid and heat, and at the same time eliminating part of the arsenic, solution of cadmium sulphate, purification of the sulphate solution, and precipitation by means of zinc or electrolysis. Three examples will be given which represent differences in preparatory treatment, and in the precipitation of cadmium by means of spelter and by means of electric current.

159. Precipitation with Spelter, Denver, Colo.—The dust is mixed with H_2SO_4 of 60°Bé. sufficient in quantity to combine with valuable base metal, for instance 10 to 15 per cent² to break up the arsenites and arsenates, and with water to form a paste. To a batch of 300 lb. dust, held in an iron box, 120 lb. acid are added and thoroughly incorporated with a hoe. Much heat is generated, fumes of HCl escape as well as H_2O vapor. After some time the mass sets as a thick mud which can be handled with a shovel. Six batches are transferred to a flue which is held at a temperature of about 230°C. After 4 days the conversion of metals into sulphates is about complete, all the moisture and a large part of the arsenic have been expelled, the mass has hardened to a cake. This is crushed to $\frac{1}{4}$ in., charged into an iron pan 2.5 ft. square, covered, and placed in a flue held at 325°C. After from 48 to 60 hr. the cakes will have been converted into a finely divided dusty powder, the conversion of metal into sulphate and the expulsion of arsenic will have progressed as far as is possible.

The powder is leached with dilute cadmium solution containing about 10 per cent CdSO_4 which is wash water from the residue. The solvent is heated to 65°C. in an agitator, e.g., a Hendryx, 400 lb. powder are gradually added and stirred for some time, say 1 hr. The solution is allowed to remain quiet for several hours until the insoluble residue has settled when the strong cadmium solution, having a specific gravity of about 1.50 and containing about 34 per

¹ "Metallurgy," transl. of Hall & Hayward, Wiley, New York, 1911.

² Hanley, *Min. Sci. Press*, 1920, CXXI, 795.

cent CdSO_4 , is siphoned off and transferred to the purifier. The insoluble residue in the agitator is agitated for some 20 min. with residue-washings from later stages of the process, and the whole flushed into settling barrels. When settled, the supernatant liquor with about 10 per cent of CdSO_4 is drawn off to serve as solvent for fresh powder. The residue is now washed on the counter-current principle until it contains less than 1 per cent of the original cadmium content, and the wash water has been enriched to about 5 per cent CdSO_4 ; this serves as washing solution for the residue from which the rich cadmium solution had been drawn off. The washed residue is transferred to a de-waterer and the resulting mud spread on a brick pavement to dry; when dry enough to be handled, it is added to a blast furnace charge as it contains 40 to 50 per cent Pb.

Purification of the strong cadmium solution with about 34 per cent CdSO_4 is essential, as, while being free from Pb, it contains As, Fe, Cu, Zn, and small quantities of other impurities. The purification vat is a wooden box, lead-lined, which has a draw-off pipe at the bottom; it is provided with a pipe for heating with live steam. The As-content of the solution is determined, the solution kept to near boiling, and 10 lb. of bluestone added for every pound of arsenic, together with some scrap iron and a little sulphuric acid. The arsenic is precipitated probably as $5\text{CuO} \cdot 2\text{As}_2\text{O}_5$, the excess Cu is taken care of by the scrap iron. The precipitate is filtered and goes to a lead blast-furnace charge. The purified solution contains a considerable amount of Fe SO_4 .

Precipitation of cadmium by means of zinc is comparatively simple. A lead-lined wooden tank of about 300 gal. capacity receives 250 gal. solution, and is heated by steam; slabs of spelter are suspended in the tank which precipitate spongy cadmium in 4 to 5 days. The liquor is waste. The cadmium sponge is drained, compressed with a car-wheel press under the pressure of 50 to 60 tons into cylinders 6 in. in diameter and 3 in. thick weighing about 131 lb. They contain 6 to 10 per cent H_2O , a little cadmium as $\text{Cd}(\text{OH})_2$ and some ZnSO_4 , also some Pb derived from spelter; they are kept under kerosene, as on exposure to air they are slowly oxidized. The cylinders cannot be melted direct in crucibles as on heating they take fire and burn. They are therefore distilled in a graphite retort such as is used in the working of silver-zinc crusts of Parkes process¹. A charge of 500 bricks is distilled in 24 hr. The retort is cooled and scraped every two weeks. The residue con-

¹ Hofman, "Lead," 1918, p. 566.

tains about 65 per cent cadmium, partly as metal but chiefly as oxide, it is added to the powder in an earlier stage of the process. The metallic cadmium is melted in a kettle and cast into sticks; the dross forming on the kettle is skimmed and charged into the retort, when it yields about 85 per cent metal.

160. Precipitation with Electric Current, Midvale, Utah.—The raw material is blast furnace dust caught in the baghouse, but not burned in the cellar. It contains about 15 per cent Cd, 20 per cent Pb, and 50 per cent As of which 35 per cent is metallic arsenic; this and the presence of carbon gives the dust a black color. An analysis of a representative sample of dust gave As 47.8, Cd 21.8, Pb 11.0, Cu 0.1, S 2.0, Zn 1.3, Fe 0.5, SiO₂ 0.4 per cent. This dust is given at a low temperature a superficial roast in a Brückner cylinder, a high temperature causes sintering; The roasted product is ground to pass a 20-mesh screen; the powder assays about 30 per cent Cd, 30 per cent Pb, and 35 per cent As. It is mixed with an equal weight of sulphuric acid of 60°Bé. and water to form a paste; the mud is shoveled into a reverberatory furnace where it is kept at a low temperature until it ceases to fume. The treated dust contains about 7 per cent As. It is leached warm with spent electrolyte containing about 3 per cent Cd, being stirred with air for about 20 min. in a Pachuca agitator to hasten dissolution and peroxidation of iron. When solution is completed, the free acid is neutralized carefully with burnt lime that has been slaked to form a powder, agitation is continued until iron and arsenic have been precipitated probably as Fe₃(AsO₄)₂, zinc as Zn(OH)₂, lead as PbSO₄; traces of copper are removed by the addition of sodium sulphide. The purified cadmium solution is filtered. The cake is bricked with miscellaneous plant dusts and goes to the blast furnace; the filtrate, containing about 8 per cent Cd and 1 to 2 per cent H₂SO₄ goes to the electrolyzing vats which are arranged as in zinc electrolysis. A vat is 3 ft. 6 in. long, 2 ft. 6 in. wide and 2 ft. 6 in. deep; it holds five cathodes, 24 by 33 in., of sheet aluminum, and six anodes, 22 by 30 in., of corroded iron on account of the presence of 1 to 3 per cent Cl in the water; the current is of 5 to 8 amp. per square foot at 3 volts. The current density is low to prevent heating of electrolyte, as when the temperature is above 20°C. the resolution of cathode cadmium is very marked, at 45°C. the cadmium is dissolved as quickly as it is deposited. The formation of trees even with this low current density can not be prevented; they are scraped off frequently from the cathode which otherwise forms a

firm deposit, once a day the scrapings are removed from a tank with a longhandled scoop. The current efficiency is 75 per cent. The further treatment of the cathode deposit is the same as at Kennett, Cal. (see §161).

161. **Precipitation with Electric Current, Kennett, Cal.**¹—The flue dust treated contains 0.55 per cent Cd, 19 Zn, 6.6 As, appreciable quantities of Te, Se, Co, Ni, Tl, and the usual metals Cu, Au, Ag, Bi, and Pb. Sulphuric-acid treatment gives a solution which

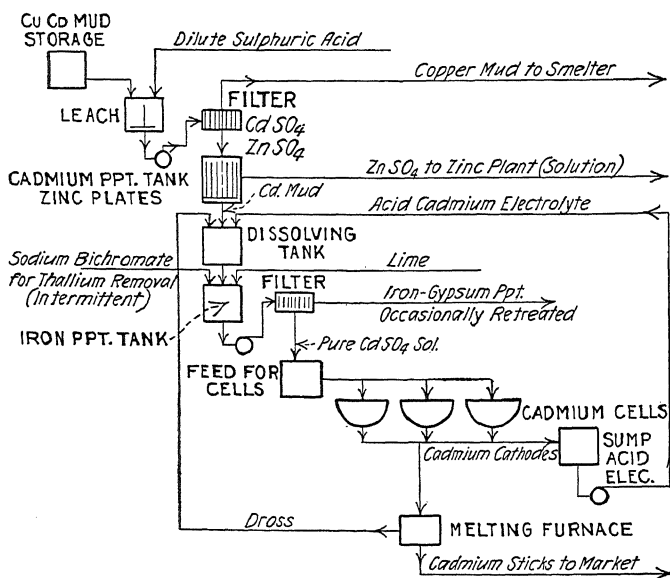


FIG. 260.—Flow sheet of cadmium plant, Kennett, Cal.

contains in grams per liter Zn 96.0, Cd 8.0, Fe 2.0, Mn 0.04, As 0.5, Bi trace, Co 0.015, Ni 0.012, Tl trace, Te trace. The solution is treated with powdered limestone and agitated with air in order to precipitate Fe and As; with these about 40 per cent of the Cu is thrown down but no Cd. To the decanted liquor is added zinc dust which gives a black precipitate containing Cu 25, Cd 25, and Zn 30 per cent, which forms the raw material for the recovery of Cd.

The flowsheet of the cadmium plant is given in Fig. 260. The precipitate, which must be kept moist to prevent oxidation of Cu,

¹ Hanley, *Chem. Met. Eng.*, 1920, XXIII, 1, 257, contains many general considerations.

is leached with dilute sulphuric acid (250 g. H_2SO_4 per liter) at a temperature of about 60°C . in a covered tank agitated with a paddle, the tank is vented to prevent gases from entering the building. When Zn and Cd have been dissolved, the solution is filtered and powdered limestone added to neutralize about 80 per cent of the free acid, which leaves the acid content about 10 g. per liter; $\text{Ca}(\text{OH})_2$ in powder form is stirred in to neutralize the remaining free acid. From the neutral zinc-cadmium solution, containing 80 g. Zn and 66 g. Cd per liter, Cd is precipitated on suspended sheet zinc (cathode zinc), spaced $2\frac{1}{2}$ in. apart in a vertical cylindrical tank 6 ft. in diameter and 5 ft. in height, provided with agitating paddles, 1 sq. ft. superficial area of zinc is adequate for 3 gal. solution; the floor of the movable rack holding the sheet zinc is solid as well as the sides for a depth of 4 in., in order to catch zinc scrap thus preventing it from falling to the bottom and contaminating precipitated cadmium sponge. The paddles revolve at 3 r.p.m. and a large clearance space is left between the paddle and the bottom of the tank, this insures a voluminous sponge precipitate, $\frac{3}{4}$ to 1 in. thickness on the plates, which is readily shaken or scraped off the sheet zinc.

The solution, from which cadmium has been precipitated to a trace, contains 80 to 118 g. Zn per liter and goes to the zinc plant.

The cadmium sponge is washed twice with warm water by decantation, drained, and shoveled into shallow wooden tanks to be dissolved in spent acid electrolyte. For the production of 300 to 400 lb. cadmium per day three tanks 6 ft. in diameter and 2.5 ft. high are required; they are tightly covered, half of the tank cover being hinged, and provided with a vent leading outside of the building (AsH_3 ?). In order to hasten solution, the liquor is maintained by means of a steam coil at 50° to 60°C ., and the mud stirred with a wooden hoe once or twice in 8 hr. When sufficient solution containing 90 to 100 g. per liter has accumulated, it is freed from Fe by neutralizing with powdery $\text{Ca}(\text{OH})_2$ and agitating with air. The purified solution is filtered and transferred to the cadmium cells.

In case there is an accumulation of Tl of over 0.3 g. per liter, this has to be removed, as it has a detrimental effect on the cadmium deposit making it spongy, reduces the current efficiency 40 to 50 per cent, and causes oxidation of cadmium in melting. This is done by the addition of sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), which precipitates from a neutral solution orange colored thallos dichrom-

ate (Ti_2CrO_4) without having any effect on the cadmium. The precipitate is removed with the iron and gypsum.

The deposition of cadmium from acid solution is carried out in cells having slowly rotating aluminum cathodes, Fig. 261, which give a smooth metallic deposit.

There are two cells in operation, with one in reserve, which are semicircular and lead-lined. A cell has nine double lead anodes between which are placed aluminum cathodes, the spacing from cathode to cathode being 9 in., so that the deposits, $\frac{1}{8}$ to $\frac{1}{16}$ in. thick can be stripped every 24 hr. without displacing the cathodes or their shafts. A stationary lead anode is entirely submerged

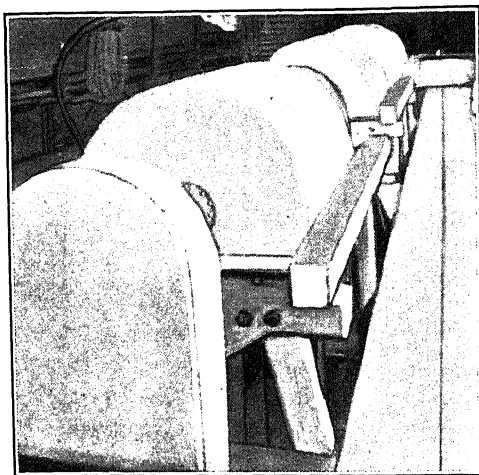


FIG. 261.—Cadmium cells with rotating cathodes.

in the electrolyte except for that portion which is connected with a copper bar connected in turn with the anode busbar. It was found necessary to connect the lining of the vat with the anode busbar by small strips of lead, as some cadmium was deposited on the lining. A rotating aluminum cathode, $\frac{3}{16}$ in. thick and 4 ft. in diameter, is riveted with aluminum rivets on a 9-in. circle to an 11-in. flange of a hub of cast aluminum, the ends of which are machined. The hubs with attached cathodes are slipped over a 4-in. steel shaft and forced into contact by the pressure of large nuts at the ends of the shaft. Electric contact is made through brushes on a pulley attached to one end of the shaft, which is rein-

forced by copper strips and faced with copper sheet. The other end of the shaft has an insulated sprocket wheel driven by a chain at 1.5 r.p.m.

A cell holds 200 gal. electrolyte to a fixed line which immerses the cathode to a depth of 18.4 in. This corresponds to 8.8 sq. ft. or 37 per cent of the area. The total immersion of the nine disks of a cell is therefore 79 sq. ft. The cells produce 113 lb. cadmium in 24 hrs., which is 85 per cent efficiency with a current of 1,200 amp. or 15 amp. per square feet cathode area, at 4 volts. There is required 1.27 kw.-hr. per pound of cadmium.

Cathodes cannot be melted as is ordinary cadmium, because there is too great a loss by oxidation; they are melted in a bath of heavy oil into bars and the bars are molded into sticks under a cover of caustic soda. Cylinder oil 650 W. is heated in a pot until white smoke comes off, cathodes are slipped into the bath slowly and melt. When 200 lb. of cathodes have been added, the oil will have been evaporated to a great extent and partly carbonized, a thin film floating on the bath of the metal which is now cast into bars weighing 50 lb. When the pot is nearly empty, the oil is ignited, suspended metal drops into the remaining bath which is cast into bars. The portion which cannot be ladled is scraped out; part of it is recovered as metal, the rest goes to the solution division. The bars are melted in a pot under a cover of caustic soda for casting sticks at a proper temperature. Bars are charged into the pot and 1.5 lb. caustic soda added. The pot is heated, the caustic melts, the bars in melting slide through the molten caustic and are protected from oxidation. The metal is now cast with the ladle having a lip to hold back the soda. The oblong mold, split on its longitudinal axis, has 17 smooth-bore holes $\frac{3}{8}$ to $\frac{1}{2}$ in. in diameter, and a gate extending across the entire top; it is similar to the one shown in Figs. 258 and 259. Moltén metal is poured into the mold previously heated; when the mold has cooled sufficiently, it is opened, the sticks are broken away from the metal on the gate, and removed for trimming and packing in boxes holding about 100 lb. The metal at the gate being hot, is fargile and easily broken. Waste metal and scrap are remelted. The loss in melting cathodes to bars is 3 to 4 per cent, and from bars to sticks, 1 to 3 per cent; the loss is mechanical, and is made good by adding shots, drosses, etc., to the solution division.

The time required to produce 400 lb. stick cadmium is given in man-hours in Table 51.

TABLE 51.—MAN-HOURS REQUIRED FOR 400 LB. STICK CADMIUM

	MAN HOURS	PER CENT
Leaching, purification and other solution preparation....	26	41.0
Cell-room operation, including stripping.....	5	9.0
Melting to bars.....	8	12.5
Melting to sticks and casting.....	16	25.0
Trimming, boxing and general work.....	8	12.5
Total.....	63	100.0

162. Preparation of Cadmium Sulphide.—This compound is valuable as a yellow pigment as it is unaffected by air, light, and hydrogen sulphide gas. It is mixed with zinc oxide or heavy spar to furnish a yellow paint (an imitation Naples yellow) with ultramarine to prepare a green pigment. In the manufacture of lithopone, the zinc sulphate is sometimes replaced in part by cadmium sulphate, and gives a yellow lithopone of varying shades.¹ It is also used in the manufacture of amber glass.

On the market there are two shades, the bright citron-yellow precipitated with hydrogen sulphide from a slightly acid solution, and the orange-yellow from a strongly acid solution. In producing the bright citron-yellow variety it is essential that the acid concentration be kept constant, and that the hydrogen sulphide bubbles be kept as much as possible out of contact with the precipitate. The vat holding the cadmium solution is charged with metallic cadmium, and the rate of precipitation is regulated that it shall not proceed more quickly than the free acid can dissolve the metal.

With the preparation of the orange-yellow sulphide such precautions are not necessary. The various shades from citron-yellow to orange-yellow can be produced by control of the free acid content of the solution. The admission of hydrogen sulphide with the citron-yellow variety is just underneath the surface of the solution.

In drying the sulphide care has to be taken, as it ignites readily. The details of manufacture are not public property.

¹ Webster, *Chem. Met. Eng.*, 1921, xxiv, 3,721.

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